09/875,158

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=> d his

     (FILE 'HOME' ENTERED AT 09:26:05 ON 07 SEP 2001)

     FILE 'CASREACT' ENTERED AT 09:26:19 ON 07 SEP 2001
L1                STRUCTURE UPLOADED
L2              2 S L1
L3                STRUCTURE UPLOADED
L4              2 S L3
L5                STRUCTURE UPLOADED
L6              2 S L5
L7             24 S L5 FULL
L8                STRUCTURE UPLOADED
L9              1 S L8
L10             4 S L8 FULL

     FILE 'REGISTRY' ENTERED AT 09:36:16 ON 07 SEP 2001
L11               STRUCTURE UPLOADED
L12               STRUCTURE UPLOADED
L13           130 S L11 FULL
L14           130 S L11  RAN=(97664-33-0,)
L15           130 S L13 OR L14
L16           164 S L12 FULL

     FILE 'CAPLUS' ENTERED AT 09:39:25 ON 07 SEP 2001
L17            60 S L15/PREP
L18            45 S L16/RCT
L19            10 S L17 AND L18

     FILE 'CASREACT' ENTERED AT 09:48:17 ON 07 SEP 2001
L20               STRUCTURE UPLOADED
L21               STRUCTURE UPLOADED
L22               STRUCTURE UPLOADED
L23             0 S L22 FULL
L24             0 S L21 FULL
L25             3 S L20 FULL

     FILE 'REGISTRY' ENTERED AT 09:50:17 ON 07 SEP 2001

     FILE 'USPATFULL' ENTERED AT 09:50:41 ON 07 SEP 2001
L26             9 S L15
L27             7 S L16
L28             2 S L26(L)L27

     FILE 'CAOLD' ENTERED AT 09:51:52 ON 07 SEP 2001
L29             9 S L15
L30            20 S L16
L31             9 S L29 AND L30
                  SEL AN 1-

     FILE 'CAPLUS' ENTERED AT 09:52:35 ON 07 SEP 2001
L32             0 S E1-E9/OREG
L33            18 S E1-E9/OREF
L34            28 S L33 OR L19
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=> d his

     (FILE 'HOME' ENTERED AT 08:48:14 ON 11 FEB 2003)

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L2              3 S L1
L3                STRUCTURE UPLOADED
L4              3 S L3
L5                STRUCTURE UPLOADED
L6              2 S L5
L7             22 S L5 FULL
L8             22 S L7 AND 1/NS
L9                STRUCTURE UPLOADED
L10               STRUCTURE UPLOADED
L11               STRUCTURE UPLOADED
L12             1 S L9 FULL SUB=L7
L13             1 S L10 FULL SUB=L7
L14             1 S L11 FULL SUB=L7
L15             2 S L12 OR L13 OR L14

     FILE 'REGISTRY' ENTERED AT 09:13:19 ON 11 FEB 2003
L16               STRUCTURE UPLOADED
L17               STRUCTURE UPLOADED
L18               STRUCTURE UPLOADED
L19               STRUCTURE UPLOADED
L20               STRUCTURE UPLOADED
L21               STRUCTURE UPLOADED
L22            31 S L16 FULL
L23           470 S L17 FULL
L24            90 S L19 FULL
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L26           129 S L22/PREP
L27           179 S L23/RCT
L28            35 S L24/RCT
L29            35 S L25/RCT
L30             1 S L26 AND L27
L31             1 S L26 AND L28
L32             1 S L26 AND L29
L33             1 S L30 OR L31 OR L32

     FILE 'USPATFULL' ENTERED AT 09:17:10 ON 11 FEB 2003
L34            35 S L22
L35            37 S L23
L36             2 S L34 AND L35
L37             5 S L24
L38             1 S L34 AND L37
L39             5 S L25
L40             1 S L34 AND L39
L41             2 S L36 OR L38 OR L40
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09/875,158

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=> file casreact
COST IN U.S. DOLLARS                                SINCE FILE      TOTAL
                                                       ENTRY    SESSION
FULL ESTIMATED COST                                    49.89     647.97

DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS)          SINCE FILE      TOTAL
                                                       ENTRY    SESSION
CA SUBSCRIBER PRICE                                    -5.88      -8.12

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FILE CONTENT:1985 - 2 Sep 2001 (VOL 102 ISS 1 - VOL 135 ISS 10)

 >>>  Several important enhancements to CASREACT functional group     <<<
 >>>  searching were introduced.  Enter HELP FGA or HELP FGC for more <<<
 >>>  information.                                                     <<<

 This file contains CAS Registry Numbers for easy and accurate
 substance identification.

Structure search limits have been increased.  See HELP SLIMIT
for details.
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09/875,158

100.0% DONE 4365 VERIFIED 0 HIT RXNS 0 DOCS
SEARCH TIME: 00.00.02

L24 0 SEA SSS FUL L21 (0 REACTIONS)

=> s l20 full
FULL SEARCH INITIATED 09:49:51 FILE 'CASREACT'
SCREENING COMPLETE - 21219 REACTIONS TO VERIFY FROM 2945 DOCUMENTS

100.0% DONE 21219 VERIFIED 8 HIT RXNS 3 DOCS
SEARCH TIME: 00.00.02

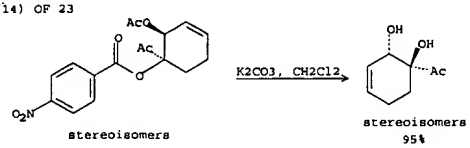
L25 3 SEA SSS FUL L20 (8 REACTIONS)

=> d scan

L25 3 ANSWERS CASREACT COPYRIGHT 2001 ACS

TI Highly selective Diels-Alder cycloadditions of captodative dienophiles 1-acetylvinyl arenecarboxylates to unsymmetrically substituted butadienes

RX(14) OF 23



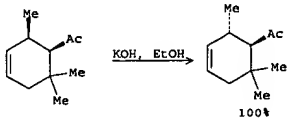
stereoisomers — stereoisomers 95%

HOW MANY MORE ANSWERS DO YOU WISH TO SCAN? (1):2

L25 3 ANSWERS CASREACT COPYRIGHT 2001 ACS

TI Preparation and scent of .delta.-damascone and its analogs

RX(3) OF 7

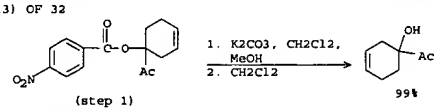


100%

L25 3 ANSWERS CASREACT COPYRIGHT 2001 ACS

TI Captodative olefin 3-(4-nitrobenzoyloxy)-3-buten-2-one as a Diels-Alder ketene equivalent for the synthesis of .gamma.-hydroxycyclohexenones

RX(13) OF 32



(step 1) — 99%

NOTE: STEREOSELECTIVE

ALL ANSWERS HAVE BEEN SCANNED

09/875,158

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COST IN U.S. DOLLARS                                SINCE FILE      TOTAL
                                                       ENTRY    SESSION
FULL ESTIMATED COST                                   264.93     912.90

DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS)          SINCE FILE      TOTAL
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CA SUBSCRIBER PRICE                                     0.00      -8.12

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STRUCTURE FILE UPDATES:    6 SEP 2001  HIGHEST RN 355113-65-4
DICTIONARY FILE UPDATES:   6 SEP 2001  HIGHEST RN 355113-65-4

TSCA INFORMATION NOW CURRENT THROUGH January 11, 2001

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  conducting SmartSELECT searches.

Structure search limits have been increased.  See HELP SLIMIT
for details.

=> d his

     (FILE 'HOME' ENTERED AT 09:26:05 ON 07 SEP 2001)
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L23             0 S L22 FULL
L24             0 S L21 FULL
L25             3 S L20 FULL

     FILE 'REGISTRY' ENTERED AT 09:50:17 ON 07 SEP 2001

=> file uspatful
COST IN U.S. DOLLARS                                SINCE FILE      TOTAL
                                                       ENTRY    SESSION
FULL ESTIMATED COST                                     0.31     913.21

DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS)          SINCE FILE      TOTAL
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CA SUBSCRIBER PRICE                                     0.00      -8.12

FILE 'USPATFULL' ENTERED AT 09:50:41 ON 07 SEP 2001
CA INDEXING COPYRIGHT (C) 2001 AMERICAN CHEMICAL SOCIETY (ACS)

FILE COVERS 1971 TO PATENT PUBLICATION DATE: 6 Sep 2001 (20010906/PD)
FILE LAST UPDATED: 6 Sep 2001 (20010906/ED)
HIGHEST GRANTED PATENT NUMBER: US6249914
HIGHEST APPLICATION PUBLICATION NUMBER: US2001020301
CA INDEXING IS CURRENT THROUGH 6 Sep 2001 (20010906/UPCA)
ISSUE CLASS FIELDS (/INCL) CURRENT THROUGH: 6 Sep 2001 (20010906/PD)
REVISED CLASS FIELDS (/NCL) LAST RELOADED: Apr 2001
USPTO MANUAL OF CLASSIFICATIONS THESAURUS ISSUE DATE: Apr 2001

>>> Page images are available for patents from 1/1/1998.  Patents   <<<
>>> and applications are typically loaded on the day of publication.<<<
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L28 ANSWER 1 OF 2 USPATFULL
ACCESSION NUMBER: 94:60291 USPATFULL
TITLE: Cyclohexene derivative and method of producing the same
INVENTOR(S): Haruta, Junichi, Yokohama, Japan
Sakuma, Kazuhiko, Yokohama, Japan
Yasuda, Akihiro, Yokohama, Japan
Hara, Katsuyoshi, Yokohama, Japan
Uchida, Itsuo, Yokohama, Japan
PATENT ASSIGNEE(S): Japan Tobacco Inc., Tokyo, Japan (non-U.S. corporation)

	NUMBER	KIND	DATE	
PATENT INFORMATION:	US 5329042		19940712	
	WO 9219582		19921112	
APPLICATION INFO.:	US 1992-955757		19921224	(7)
	WO 1992-JP537		19920424	
			19921224	PCT 371 date
			19921224	PCT 102(e) date

	NUMBER	DATE
PRIORITY INFORMATION:	JP 1991-188377	19910426
	JP 1991-188378	19910426

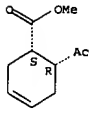
DOCUMENT TYPE: Utility
FILE SEGMENT: Granted
PRIMARY EXAMINER: Killos, Paul J.
LEGAL REPRESENTATIVE: Birch, Stewart, Kolasch & Birch
NUMBER OF CLAIMS: 17
EXEMPLARY CLAIM: 1
LINE COUNT: 886
CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB Provided is a novel (1R, 2S)-1-acyl-2-carboxycyclohex-4-ene derivative represented by the following general formula [I], and its producing method, ##STR1## (where R.sup.1 represents a hydrogen atom, a lower alkyl group, or substituted or unsubstituted aryl group, and R.sup.2 represents a hydrogen atom, or a lower alkyl group). Also provided is a method of producing a (3S, 4R)-4-substituted-3-carboxycyclopentanone derivative represented by the following general formula [A], ##STR2## (where R.sup.1 and R.sup.2 are the same as those mentioned above).

IT **146388-95-6P**
(prepn. of, in prepn. of intermediate for TSH-releasing hormone deriv.)
RN 146388-95-6 USPATFULL
CN 3-Cyclohexene-1-carboxylic acid, 6-acetyl-, methyl ester, (1S-cis)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.

L28 ANSWER 1 OF 2 USPATFULL (Continued)



L28 ANSWER 2 OF 2 USPATFULL
ACCESSION NUMBER: 88:47257 USPATFULL
TITLE: Isopropyl-methyl-butenoyl-cyclohexanes, -cyclohexenes and -cyclohexadienes, and also perfume compositions and
perfumed articles and materials which contain said compounds as a perfume ingredient
INVENTOR(S): Van Der Weerdt, Antonius J. A., Huizen, Netherlands
Broekhof, Nicolaas L. J., Naarden, Netherlands
Witteveen, Jan G., Naarden, Netherlands
PATENT ASSIGNEE(S): Naarden Intl. N.V., Netherlands (non-U.S. corporation)

	NUMBER	KIND	DATE	
PATENT INFORMATION:	US 4760050		19880726	
APPLICATION INFO.:	US 1987-2391		19870109	(7)

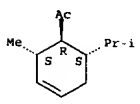
	NUMBER	DATE
PRIORITY INFORMATION:	NL 1986-152	19860123

DOCUMENT TYPE: Utility
FILE SEGMENT: Granted
PRIMARY EXAMINER: Reamer, James H.
LEGAL REPRESENTATIVE: Brumbaugh, Graves, Donohue & Raymond
NUMBER OF CLAIMS: 16
EXEMPLARY CLAIM: 1
LINE COUNT: 407
CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB 1-Isopropyl-3-methyl-2-(but-2'-enoyl)cyclohexane derivatives having the general formula ##STR1## in which the dotted lines represent no double bond, one double bond at position 4 or two double bonds at positions 1 and 5, 2 and 4 or 4 and 6 are valuable fragrances with fruity flowery and green odors, in some cases accompanied by woody and/or herbal notes.
Above defined compounds can be used as a perfume component in perfume compositions or in products to be perfumed.

IT **115865-78-6P 115938-79-9P**
(prepn. and aldol reaction of, with acetaldehyde)
RN 115865-78-6 USPATFULL
CN Ethanone, 1-[2-methyl-6-(1-methylethyl)-3-cyclohexen-1-yl]-, (1.alpha.,2.beta.,6.beta.)- (9CI) (CA INDEX NAME)

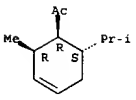
Relative stereochemistry.



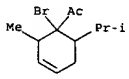
RN 115938-79-9 USPATFULL
CN Ethanone, 1-[2-methyl-6-(1-methylethyl)-3-cyclohexen-1-yl]-, (1.alpha.,2.alpha.,6.beta.)- (9CI) (CA INDEX NAME)

Relative stereochemistry.

L28 ANSWER 2 OF 2 USPATFULL (Continued)



IT **115865-81-1P**
(prepn. and dehydrohalogenation of)
RN 115865-81-1 USPATFULL
CN Ethanone, 1-[1-bromo-2-methyl-6-(1-methylethyl)-3-cyclohexen-1-yl]- (9CI) (CA INDEX NAME)



09/875,158

=> d ibib ab hitstr 1-18 l33

L33 ANSWER 1 OF 18 CAPLUS COPYRIGHT 2001 ACS
ACCESSION NUMBER: 1961:13111 CAPLUS
DOCUMENT NUMBER: 55:13111
ORIGINAL REFERENCE NO.: 55:2517g-i,2518a-i,2519a-b
TITLE: The synthesis of substituted 1-methylcyclohexanecarboxylic acids and the stereochemistry of the Favorskii rearrangement
AUTHOR(S): Stork, Gilbert; Borowitz, Irving J.
CORPORATE SOURCE: Columbia Univ.
SOURCE: J. Am. Chem. Soc. (1960), 82, 4307-15
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

AB The stereoelectronic requirements of the Favorskii reaction were examd. It was concluded that the formation of the cyclopropanone intermediate was concerted, at least in the case of 1-chloro-1-acetylcyclohexane (I), in disagreement with the proposal by Burr and Dewar (CA 48, 8601f). Some extensions of the reaction were also described. 2-Chlorocyclohexanone (3.3 g.) added during 0.5 hr. to 3.6M PhCH2ONa in PhCH2OH, the mixt. concd. in vacuo, dild. with H2O to make the soln. 10% in aq. NaOH, heated 2 hrs. on the steam bath under N, and the product isolated yielded 75% cyclopentanecarboxylic acid. A series of similar runs with various Na alkoxides showed that the yields of acid decreased in the order PhCH2ONe, EtONa, MeONa, iso-PrONa. PhCH2ONa from 1.42 g. Na in 20 cc. dry Et2O and 2.8 g. I stirred 17 hrs. at room temp., the mixt. evapd., and the residue refluxed 48 hrs. under N with 5 cc. H2O yielded 72% 1-methylcyclohexanecarboxylic acid (II). 2-Chloro-2-methylcyclohexanone could not be rearranged with PhCH2ONa, EtONa, or MeONa in the corresponding alcs. 2-Methylcycloheptanone, b. 178-83.degree., n29D 1.4528 (2,4-dinitrophenylhydrazone m. 111.0-12.5.degree.), was obtained (63%) from cyclohexanone with MeCHN2, converted to 56% 2-methyl-2-chlorocycloheptanone, b2 65-6.degree., n24D 1.4790, a 12.15-g. portion of this added during 28 min. to 6.15 g. Na in 76 cc. dry PhCH2OH, the mixt. shaken 1.75 hrs. at room temp., dild. with 80 cc. iced H2O, and the product isolated with Et2O gave 6.88 g. PhCH2 ester (III) of II. III (3.0 g.) in 24 cc. EtOAc contg. 1 drop concd. H2SO4 hydrogenated over 0.23 g. 10% Pd-C during 5.75 hrs. yielded 1.41 g. II; anilide m. 110.2-11.4.degree. (C6H6); the original basic aq. soln. gave an addnl. 2.1 g. II. 2-Methylcycloheptenone (3.0 g.), b. 87-9.degree. (2,4-dinitrophenylhydrazone m. 121-2.degree.), added to 0.080 g. Na in 8 cc. dry EtOH and 3.67 cc. CH2(CO2Et)2, the mixt. kept 20 hrs. under N at room temp., evapd., treated with 6.05 cc. glacial AcOH, 3.1 cc. concd. HCl, and 1.5 cc. H2O, refluxed 24 hrs., evapd. at 100.degree./20 mm., treated with 2 cc. concd. H2SO4 and 20 cc. MeOH, kept 24 hrs. at room temp., and worked up yielded 2.39 g. Me 2-methyl-3-oxocycloheptaneacetate, b0.3 105-25.degree. (bath); 2,4-dinitrophenylhydrazone, orange, m. 150.2-2.2.degree. (MeOH-CHCl3). Me trans-2-methyl-2-chloro-3-oxocycloheptaneacetate, b0.1 102-25.degree., rearranged with KOH in abs. EtOH and the product hydrogenated catalytically yielded 15% trans-2-methyl-2-carboxycyclohexaneacetic acid, m. 173.4-76.0.degree. (Me2CO-pentane). Methylcyclohexene, b. 105-6.degree., converted in 40% yield to a mixt., b16 110-15.degree., of 1-acetyl-2-methyl-1-cyclohexene and 1-acetyl-2-methyl-2-cyclohexene, a 23.3-g. portion in 50 cc. abs. EtOH contg. 1 pellet KOH rearranged in the usual manner, and the mixt. hydrogenated over 1.8 g. 10% Pd-C yielded 45% mixt., b16 75-80.degree., of cis- and trans-1-acetyl-2-methylcyclohexane; a 10.0 g. portion of the mixt. with 6.9 cc. SO2Cl2 yielded 2.16-3.83 g. cis-1-acetyl-1-chloro-2-methylcyclohexane (IV), b14 88-95.degree., n24.5D 1.4707, and a mixt. of mono- and dichloroketones, b9 90-100.degree., n24.5D 1.4794. 2-Oxo-3-acetyl-4-methylbutyrolaetone-H2O (26.0 g.), m. 89-93.degree., prepd. in 75% yield from Na ethylacetopyruvate and AcH, in 57 cc. MeOH and 81 cc. H2O treated with stirring at 10-15.degree. with 11.3 g. Cl during 30 min., the mixt. neutralized with 53 g. KHCO3 in 105 cc. H2O, and worked up gave 74% MeCH:CClAc (V), b23 55-7.degree., n21D 1.4702; 2,4-dinitrophenylhydrazone, red, m. 198.8-9.5.degree. (CHCl3). V (4.0 g.), 12 cc. (CH2:CH)2, and a few mg. hydroquinone in a sealed tube heated 2 hrs. at 160.degree. and 24 hrs. at 130.degree. and 2 such runs combined and worked up yielded 6.23 g. 1-acetyl-1-chloro-2-methyl-4-cyclohexene (VI), b2.5 68-9.degree.. VI (4.0 g.) in 30 cc. cyclohexane hydrogenated 14.5 hrs. over 0.16 g. 10% Pd-C yielded 72-82% trans-isomer (VII) of IV, b16 85-7.degree., n24.5D 1.4707. VII (13.87 g.) in 30 cc. MeOH treated 14 hrs. at 5-10.degree. with 1.7 g. NaBH4 yielded 11.18 g. trans-1-(1-hydroxyethyl) analog (VIII) of VII, b4.5 85-91.degree.. The VIII refluxed 42 hrs. with 3.2 equivs. KOH in MeOH and distd. and the resulting epoxide refluxed 5 hrs. in tetrahydrofuran with 4.9 equivs. LiAlH4 yielded 73-81% 1-Et analog of VII, b28 125-30.degree., which refluxed 22 hrs. in C6H6 under N with 2 equivs. PBr3, worked up, and then refluxed 17 hrs. under N with 2 equivs. NaOH in EtOH gave 1.49 g. 1-ethyl-2-methylcyclohexene. V (2.0 g.) and 2 cc. MeCH:CH)2 (IX) heated in a sealed tube with a little hydroquinone 19.5 hrs. at 130.degree. yielded 68-74% 1-acetyl-1-chloro-2,3,5-trimethyl-4-cyclohexene (X), b0.6 67-9.degree., n19.5D 1.4905. trans-Crotonic acid chlorinated in 88% yield to MeCHClCHClCO2H, m. 50-2.degree., and then dehydrochlorinated with C5H5N gave 65% trans-MeCH:CClCO2H (XI), m. 99-100.degree.. XI (25 g.) and 67.5 cc. PhCH2OH in 300 cc. dry C6H6 contg. 0.15 g. p-MeC6H4SO3H refluxed 24 hrs. under N yielded 60% PhCH2 ester (XII) of XI, b3.5 131.degree.. XII (28.3 g.) and 12.7 g. IX in a sealed tube heated 24 hrs. at 170.degree. with a little hydroquinone gave 72% adduct, b0.1 125-30.degree.; a 0.7-g. portion in 14 cc. cyclohexane hydrogenolyzed 28 min. over 0.113 g. 10% Pd-C yielded 0.226 g. trans-1-chloro-2,4,5-trimethyl-4-cyclohexenecarboxylic acid (XIII), m. 102.4-3.1.degree. (sublimed at 70.degree./3 mm.). XIII (5.01 g.), 2 cc. SOCl2, and 10 cc. dry C6H6 refluxed 8.5 hrs., the resulting acid chloride added to CH2N2-Et2O from 15.1 g. H2NCON(NO)Me, the mixt. kept 12 hrs. at room temp., evapd., the crude diazo ketone in 25 cc. dry Et2O kept 20 hrs. with 1.2 g. dry HCl in 13 cc. Et2O, and worked up gave 4.88 g. dichloroketone, light yellow oil; a 4.88-g. portion in 20 cc. abs. EtOH and 80 cc. C6H6 contg. 2 drops glacial AcOH treated with 3.72 g. NaI yielded 2.47 g. X, b4.5-5.5 97-9.degree., n25D 1.4882. IV (1.4 g.) added with stirring to dry PhCH2ONa from 0.92 g. Na in dry Et2O, the mixt. stirred 12 hrs. at room temp., dild. with 10 cc. H2O, refluxed 48 hrs., and worked up gave 44% cis-1,2-dimethylcyclohexanecarboxylic acid (XIV), b8 160-70.degree. (bath); anilide m. 115.6-16.1.degree. (cyclohexane). Tiglic acid (XV) (3.0 g.), m. 63.5-65.degree., and 9 cc. (CH2:CH)2 in a sealed tube heated 27 hrs. at 190-200.degree. with a little hydroquinone, distd., and the distillate (2.66 g.), b0.5 160.degree., hydrogenated in EtOAc over 0.1 g. PtO2 gave 0.77 g. XIV, m. 115.4-16.6.degree.. VII rearranged in the usual manner yielded 30% trans-isomer of XIV, b9 150-60.degree.; anilide m. 81.4-2.6.degree. (cyclohexane). X (1.52 g.) (from V) rearranged with dry PhCH2ONa yielded 0.92 g. trans-1,2,4,5-tetramethyl-4-cyclohexenecarboxylic acid (XVI), m. 80.0-1.6.degree. (chromatographed on silica gel-Celite) (sublimed at 70.degree./2 mm.). X (from XI) gave similarly 20-8% XVI. XV (1.0 g.), 2.0 cc. (MeCH:CMe)2, and a little hydroquinone heated 24 hrs. in a sealed tube at 180.degree. and the crude product (1.25 g.) chromatographed on 1:1 silicic acid-Celite yielded the cis-isomer of XVI, m. 86.0-7.0.degree..

L33 ANSWER 2 OF 18 CAPLUS COPYRIGHT 2001 ACS
ACCESSION NUMBER: 1961:13110 CAPLUS
DOCUMENT NUMBER: 55:13110
ORIGINAL REFERENCE NO.: 55:2517c-g
TITLE: Compounds with urotropine structure. XIX. .beta.-(1-Adamantyl)-.beta.-oxopropionic acid ethyl ester
AUTHOR(S): Stetter, Hermann; Rauscher, Elli
CORPORATE SOURCE: Univ. Munich, Germany
SOURCE: Chem. Ber. (1960), 93, 2054-7
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

AB cf. CA 54, 20912c. A series of reactions of Et 3-(1-adamantyl)-3-oxopropionate (I), readily obtainable from adamantane-1-carboxylic acid chloride (II) and EtOCH(CO2Et)2, was described. Activated Mg (3.6 g.) treated with 11 cc. dry C6H6 and 1 cc. abs. EtOH, the mixt. treated with 24.0 g. CH2(CO2Et)2, 7.0 g. abs. EtOH, and 30 cc. dry C6H6, refluxed to soln., evapd., the residue treated with cooling and stirring with 19.8 g. II in 30 cc. dry C6H6 during 30-40 min., refluxed 1 hr. with stirring, dild. with ice and dil. H2SO4, and the C6H6 layer worked up gave 80-5% I, b0.06 108-10.degree.. I (1.0 g.), 1 cc. PhNHNH2, 4 cc. glacial AcOH, and 2 cc. H2O kept 3 hrs. at room temp. gave 0.8 g. 1-phenyl-3-(1-adamantyl)-5-pyrazolone, m. 138-9.degree. (EtOH). Crude I (25 g.), 50 cc. glacial AcOH, 30 cc. H2O, and 5.5 cc. concd. H2SO4 refluxed 3-4 hrs., cooled, and poured into 300 cc. iced H2O yielded 94-6% Me 1-adamantyl ketone (III), m. 53-4.degree. (aq. MeOH); oxime, leaflets, m. 182-4.degree. (aq. dioxane); 2,4-dinitrophenylhydrazone, orange needles, m. 219-20.degree. (EtOH). III (8.9 g.) in 100 cc. dry Et2O reduced with 1.5 g. LiAlH4 in 75 cc. Et2O gave 8.5 g. .alpha.-(1-adamantyl)ethanol, needles, m. 75-6.degree.. III (8.9 g.) in 20 cc. abs. EtOH with 8 g. Br in the presence of a small amt. of AlBr3 yielded 10.1 g. bromomethyl 1-adamantyl ketone (IV), m. 78-9.degree. (MeOH). I (15 g.) stirred 1-2 days with 1.4 g. powd. Na in 150 cc. Et2O, treated dropwise with stirring during 2 hrs. with 15.5 g. IV, refluxed 1-2 hrs. with stirring, filtered, evapd., the sirupy residue refluxed 4 hrs. with 3 g. KOH in 120 cc. MeOH, and cooled yielded 9.2 g. 1,4-di(1-adamantyl)butane-1,4-dione (V), leaflets, m. 132-3.degree. (MeOH). V (1.0 g.) in 10 cc. concd. H2SO4 kept 15 hrs. at room temp. yielded 0.8 g. 2,5-di(1-adamantyl)furan, m. 217.degree. (EtOH). V (3.5 g.), 2 g. NH3, and 10 cc. MeOH heated 7 hrs. in a sealed tube at 125.degree. gave 3.2 g. 2,5-di(1-adamantyl)pyrrole, m. 227-8.degree. (EtOH).

L33 ANSWER 3 OF 18 CAPLUS COPYRIGHT 2001 ACS
ACCESSION NUMBER: 1960:128473 CAPLUS
DOCUMENT NUMBER: 54:128473
ORIGINAL REFERENCE NO.: 54:24503h-i,24504a
TITLE: Preparation of o-diacetylbenzene by the Diels-Alder reaction
AUTHOR(S): Maekawa, Etsuro
CORPORATE SOURCE: Tech Hochschule, Syowaku, Nagoya
SOURCE: Bull. Chem. Soc. Japan (1960), 33, 205-8
DOCUMENT TYPE: Journal
LANGUAGE: German

AB A red color, changing slowly to violet, was formed when o-diacetylbenzene was added to primary amines, hence its use in paper chromatography; detection of 20-50 .gamma. of amino acids or 1 .gamma. of aromatic primary amines was possible. .alpha.,.beta.-Diacetylethylene (I) (40 g.) in 300 ml. EtOH, refluxed with 50 g. 1-acetoxy-1,3-butadiene (II) 24 hrs. (moisture-free) and the solvent evapd. in vacuo, yielded a residue which, after fractionating twice iv vacuo, gave 65 g. 3-acetoxy-1,2,3,6-tetrahydro-1,2-diacetylbenzene (III) b12 156-9.degree., this gave with PhNH2 in AcOH a red color in the cold, changing slowly to violet. III (25 g.) heated 5 hrs. with 3.5 g. S at 100 mm. at 160-80.degree. gave, with rapid formation of H2S and AcOH, a mixt. which, after distn. in a high vacuum, yielded 18 g. light yellow o-diacetylbenzene (IV), b0.05 105.degree.. The oil gave an intense violet color in the cold and crystd. in part (after long chilling) in needles, m. 37.degree.; disemicarbazone m. 150.degree.. III and O2 of air or NaHCO3 soln. gave little or no IV, shown by color reaction or disemicarbazone formation. In the attempted prepn. of 3-acetoxy-1,2-diacetylbenzene from a dibromo deriv. of III, an impure product was formed in poor yield, which this gave a violet color with the above reagents.

L33 ANSWER 4 OF 18 CAPLUS COPYRIGHT 2001 ACS
ACCESSION NUMBER: 1960:128472 CAPLUS
DOCUMENT NUMBER: 54:128472
ORIGINAL REFERENCE NO.: 54:24503a-h
TITLE: Synthesis of a homolog of dihydroxyephedrine
AUTHOR(S): Lespagnol, Albert; Cuingnet, Etienne
CORPORATE SOURCE: Fac. med. pharm., Lille, Fr.
SOURCE: Ann. pharm. franc. (1960), 18, 445-53
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

AB Adding to refrigerated 133.5 g. AlCl3 in 400 cc. CS2 dropwise 138 g. veratrole in 92.5 g. propionyl chloride with the temp. maintained at 0-5.degree. and with stirring, keeping overnight, decanting, adding to the solid 500 cc. H2O and ice, extg. the oil with C6H6, washing the ext. with 10% NaOH, drying, evapg. and distg. at 188.degree./20 mm. gave 118 g. 3',4'-dimethoxypropiophenone (Ia), m. 57.5.degree.. The same compd. was prepd. in 65% yield in C6H6, b0.8 140.degree.. Adding to 97 g. Ia in 300 cc. refluxing Et2O 80 g. Br dropwise, refluxing 10 min., evapg. partially in vacuo, adding 500 cc. cyclohexane, heating to evap. the rest of the Et2O, cooling, keeping overnight at 10.degree., washing twice with cold cyclohexanol satd. with MeOH, and drying gave 112 g. 2-bromo-3',4'-dimethoxypropiophenone (I), m. 88.degree.. Stirring at room temp. 130 g. I, 250 cc. MeOH, and 187 g. 30% EtNH2 in H2O in a closed container 45 min., keeping at 37.degree. for 12 hrs., evapg. in vacuo to beginning crystal formation, cooling, adding 200 cc. 30% NaOH, dissolving the oil formed in 150 cc. Et2O, drying on K2CO3, evapg., dissolving the residue in 300 cc. Me2CO, treating with dry HCl gas, filtering and washing with Me2CO gave 97 g. 2-ethylamino-3',4'-dimethoxypropiophenone-HCl (II), m. 234.degree., b0.5 144-5.degree.. Adding to refrigerated 60 g. AlCl3 in 120 g. PhNO2 26.9 g. 2-ethylaminopropionitrile-HCl, keeping between 20 and 30.degree., adding 27.6 g. veratrole and passing dry HCl through the mixt. during 6 hrs., keeping 24 hrs., pouring into 200 cc. water and ice, refluxing 10 min., allowing to cool slowly, keeping overnight, filtering off the crystals, and recrystg. from Me2CO-MeOH gave quickly formed crystals and light crystals depositing slowly. The latter were not investigated. Decanting when the light crystals began to appear gave 25% II. Hydrogenating 21.5 g. II in 100 cc. EtOH in the presence of 1 g. PtO2 at room temp. and 1 atm., sepg. the catalyst, evapg. the solvent, dissolving the oily residue in 100 cc. Me2CO, adding HCl in EtOH to acid reaction and keeping refrigerated overnight gave 20 g. 2-ethylamino-1-(3,4-dimethoxyphenyl)-1-propanol-HCl (III), m. 209.degree. (Me2CO-MeOH). Alkalinizing the concd. soln. of III in H2O gave an oil, crystg. slowly, giving the base of III, m. 81-2.degree. (cyclohexane-iso-Pr2O). Heating 97 g. II and 300 cc. 48% HBr, then refluxing 3 hrs., cooling under CO2, removing the HBr and H2O in vacuo, dissolving the residue under CO2 in 250 cc. MeOH, boiling 5 min. with C, filtering while hot under CO2, adding peroxide-free Et2O, cooling, shaking in contact with dry NH3 until the odor of NH3 persisted, filtering and washing with Me2CO gave a mixt. of NH4Br with 2-ethylamino-3',4'-dihydroxypropiophenone (IV). Triturating the mixt. with 100 cc. cold H2O,

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AB washing 5 times with 20 cc. cold. H2O and drying in vacuo gave 55 g. IV, m. 177-8.degree. (PrOH). IV was also obtained by heating 10 g. II in 30 cc. HCl 3 hrs. in a sealed tube at 160.degree.. Hydrogenating 24 g. IV in 125 cc. AcOH and 25 cc. H2O with 4 g. 10% Pd-C at 20-5.degree. and 1 atm. during 12 hrs., sepg. the catalyst, concg. the soln. at 70.degree. to 0.5 vol., cooling, adding 150 cc. Me2CO, passing with cooling dry HCl gas through the soln., keeping 2 hrs. in the cold, and washing the ppt. with Me2CO gave 24.5 g. 2-ethylamino-1-(3,4-dihydroxyphenyl)-1-propanol-HCl, which, purified by dissolving in 200 cc. MeOH, filtered, evapd. to 1/2 vol. pptd. with peroxide-free Et2O, kept at 0.degree. for 4 hrs., filtered and washed with Me2CO, gave 17 g. pure product, m. 212-14.degree. (decompg.).

L33 ANSWER 5 OF 18 CAPLUS COPYRIGHT 2001 ACS
ACCESSION NUMBER: 1960:1923 CAPLUS
DOCUMENT NUMBER: 54:1923
ORIGINAL REFERENCE NO.: 54:375g-i,376a-f
TITLE: Acyl derivatives of cyclic compounds. V. The preparation of o-diacetylbenzene and 4-nitro-1,2-diacetylbenzene
AUTHOR(S): Riemschneider, Randolph; Kassahn, Horst G.
CORPORATE SOURCE: Freie Univ., Berlin
SOURCE: Chem. Ber. (1959), 92, 1705-9
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

AB cf. C.A. 46, 5549c; 50, 731a. Phthalic anhydride (74 g.) and 62 g. CH2(CO2H)2 heated 7 hrs. on the water bath with 48 cc. C5H5N, dild. warm with 420 cc. H2O and filtered, the filtrate treated with 24 cc. concd. HCl, kept 3 days at room temp., and filtered, and the residue dried gave 34.5 g. o-AcC6H4CO2H (I), m. 114-15.degree.; the filtrate dild. with 25 cc. concd. HCl and refrigerated 24 hrs. gave 5.9 g. 2nd crop; the aq. solns. evapd. in vacuo and the residue extd. with Et2O yielded an addnl. 2.3 g. I. I (35 g.), 175 cc. glacial AcOH, 17.5 g. red P, 6.2 g. iodine, and 25 cc. HI refluxed 25 hrs. with stirring, filtered, added with stirring to 15 g. NaHSO3 in 500 cc. H2O, cooled, and filtered yielded 30 g. o-EtC6H4CO2H (II), m. 68.degree.. II (30 g.) treated with cooling with 28.5 g. SOCl2, refluxed 1.5 hrs., and distd. yielded 33.2 g. o-EtC6H4COCl (III), b. 226.degree.. Mg (5.35 g.), 5 cc. abs. EtOH, and 0.5 cc. CCl4 warmed to initiate the reaction, the mixt. treated after 5 min. during 0.5 hr. with 90 cc. dry Et2O, heated on the water bath, treated dropwise with stirring with 35.2 g. CH2(CO2Et)2, 20 cc. abs. EtOH, and 25 cc. dry Et2O, refluxed 3 hrs. with stirring, treated dropwise with stirring and gentle warming with 33.2 g. III in 45 cc. dry Et2O, refluxed 1.5 hrs. with stirring, cooled, acidified with stirring with dil. H2SO4, the aq. phase extd. with Et2O, the combined Et2O exts. worked up, the residual yellow oil refluxed 7 hrs. with 60 cc. glacial AcOH, 7.5 cc. concd. H2SO4, and 40 cc. H2O, cooled, basified with 20% aq. NaOH, and extd. with Et2O yielded 26.5 g. o-EtC6H4Ac (IV), b18 108.degree.. AcCH2CH(OH)Et dehydrated to EtCH:CHAc and then condensed with (CH:CH2)2 in an autoclave at 150.degree. yielded up to 35% 4-ethyl-5-acetylcyclohexene, b20 98-101.degree., which, refluxed several hrs. with Pd-C, gave IV. IV (7.5 g.) in 120 cc. H2O treated with stirring at 65.degree. with 25.5 g. Mg(NO3)2.6H2O and 12.5 g. KMnO4 during 4 hrs. and worked up in the usual manner yielded 3.4 g. unchanged IV and 2.6 g. o-C6H4Ac2 (V), b20 148.degree., m. 39.degree. (pert. ether); similar runs with 145 cc. and 320 cc. H2O yielded 2.4 and 0.6 g. V, resp.; bis(2,4-dinitrophenylhydrazone) m. 211.degree. (decompn.). o-C6H4(CH(OH)Me)2 (5 g.), m. 108.degree., oxidized in the same manner gave 3.5 g. oil, b0.01-0.03 110-13.degree., which yielded pure V only with difficulty. II (25 g.) in 50 cc. glacial AcOH treated with cooling and stirring dropwise during 3 hrs. with 35 g. HNO3 (d. 1.4) and 56 g. concd. H2SO4, stirred 1 hr. at 70.degree., poured into 250 cc. iced H2O, filtered, and the residue of mixed isomers recrystd. from boiling H2O yielded 5.5 g. 2,4-Et(O2N)C6H3CO2H (VI), m. 130.degree., and 22.5 g. 2,5-isomer (VII) of VI, m. 164.degree.. VI (9.8 g.) refluxed 3 hrs. with 8.3 g. SOCl2, evapd., and distd. gave 9.9 g. 2,4-Et(O2N)C6H3COCl (VIII), b8 183-4.degree., n20D 1.5667. VII yielded similarly the 2,5-isomer (IX) of VIII, b8 194-6.degree., n20D 1.5691. Mg (1.36 g.), 1.25 cc. abs. EtOH,

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0.15 cc. CCl4, and 25 cc. dry Et2O treated in the usual manner with 8.8 g.
CH2(CO2Et)2 in 5 cc. abs. EtOH and 6.5 cc. dry Et2O, the mixt. treated dropwise with stirring during 45 min. with 10.7 g. VIII in 30 cc. dry Et2O, heated 1 hr. with stirring, cooled, and acidified with dil. H2SO4, the aq. phase extd. with Et2O, the combined Et2O solns. worked up, the residual oil refluxed 7 hrs. with 15 cc. glacial AcOH, 1.9 cc. concd. H2SO4, and 10 cc. H2O, cooled, basified with 20% aq. NaOH, and the product isolated with Et2O gave 6.9 g. 2,4-Et(O2N)C6H3Ac (X), b3 141-4.degree., n20D 1.5509; semicarbazone m. 230-2.degree.. IX (10.7 g.) yielded similarly 6 g. 2,5-isomer (XI) of X, b8 192.degree., n20D 1.5537; semicarbazone m. 234-6.degree.. X (6 g.) in 30 cc. C5H5N treated (at 70.degree. with stirring) gradually with 11.5 g. AgMnO4 in 120 cc. C5H5N, cooled, and filtered, the residue washed with 20 cc. C5H5N, the combined filtrates concd. to 30 cc., and the residue dissolved in 150 cc. Et2O, washed, dried, and distd. gave 3.2 g. 4,1,2-O2NC6H3Ac2 (XII), b4 144-7.degree., which was also obtained similarly from XI.

L33 ANSWER 6 OF 18 CAPLUS COPYRIGHT 2001 ACS
ACCESSION NUMBER: 1959:50856 CAPLUS
DOCUMENT NUMBER: 53:50856
ORIGINAL REFERENCE NO.: 53:**9093h-i,9094a-d**
TITLE: Synthesis of 2-acetyl-3-carbomethoxybicyclo[2.2.1]hept-5-enes and of 1-acetyl-2-carbomethoxy-4-cyclohexene diastereoisomers
AUTHOR(S): Mousseron, Max; Jacquier, Robert; Soulier, Jacques
SOURCE: Compt. rend. (1958), 247, 665-8
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
AB The endo-cis-and exo-cis-anhydrides of bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid (I) heated with anhyd. MeOH give the endo-cis- and exo-cis-acid esters, m. 99.degree. and 66.degree., resp. SOCl2 in Et2O gives with the latter monochlorides of the corresponding acids without inversion; treatment with H2O regenerates the acid esters. CdMe2 with I gives 60% endo-cis- and exo-cis-2-acetyl-3-carbomethoxybicyclo[2.2.1]hept-5-enes (II), b14 148-50.degree. and b17 147-8.degree., resp.; 2,4-dinitrophenylhydrazones (DNP) m. 102.degree. and 122-3.degree., resp. Sapon. with boiling 30% NaOH causes inversion of the configuration on the C atom bearing the Ac group. The endo-cis-II gives a ketonic acid (III), m. 101.degree., which treated with iodine in the presence of Na2CO3 forms an iodolactone from which it is regenerated with Zn-HOAc, showing the acid group to be in the endo position. With CH2N2 the diastereoisomer (DNP m. 102-3.degree.) forms rather than endo-cis-II. With NaBrO III gives bicyclo[2.2.1]hept-5-ene-2,3-trans-di-carboxylic acid (IV), m. 190.degree.. Exo-cis-II sapond. gives a ketonic acid, m. 122.degree., which forms no iodolactone; it is esterified with CH2N2 (DNP m. 135-6.degree.) and gives IV by a haloform reaction. By treating trans-.beta.-acetylacrylic acid (V) with cyclopentadiene, a mixt. of acids, m. 80-5.degree., forms; reduction of the iodolactones from this mixt. with Zn and HOAc gives III; the diastereoisomer has been isolated from the mother liquor. The pyrolysis of endo-cis-II gives the Me ester of V m. 60.degree.; DNP m. 204-5.degree.. In the cyclohexene series, the cis-mono-Me ester, m. 80.degree., obtained from the anhydride, is successively transformed without inversion to the acid chloride, then with CdMe2 to cis-1-acetyl-2-carbomethoxy-4-cyclohexene (VI), b16 140-1.degree.; DNP m. 127.degree.. Sapon. with 30% NaOH occurs without inversion. The trans structure of 1-acetyl-4-cyclohexene-2-carboxylic acid (VII), m. 113-14.degree., thus isolated is demonstrated as follows: it is identical with the product of condensation of butadiene and V; it gives with CH2N2 an ester (DNP m. 128.degree., mixed m.p. of DNP with that from VI 105-10.degree.); by a haloform reaction, trans-4-cyclohexene-1,2-dicarboxylic acid, m. 172.degree. (anhydride m. 186.degree.), forms. VI with MeMgBr gives cis-3,3-dimethyl-1,3,4,7,8,9-isobenzofurane, m. 67-8.degree., 5.60 .mu. (.gamma.-lactone), 6.01 .mu. (C:C), doublet at 7.19 and 7.26 .mu. (gem-dimethyl group) (CHCl3). The isomer, m. 114.degree., has been obtained analogously (Dixon and Wiggins, C.A. 49, 1564g). These products are identical with those m. 70.degree. and 114.degree. obtained by Sopov (C.A. 51, 1868i) from MeMgBr and cis- and trans-1,2-dicarbethoxy-4-cyclohexenes, considered to be 1,2-diacetyl-4-cyclohexene diastereoisomers.

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L33 ANSWER 7 OF 18 CAPLUS COPYRIGHT 2001 ACS
ACCESSION NUMBER: 1959:50855 CAPLUS
DOCUMENT NUMBER: 53:50855
ORIGINAL REFERENCE NO.: 53:**9091e-i,9092a-i,9093a-h**
TITLE: Base-catalyzed dimerization of 3-substituted cyclohexenones
AUTHOR(S): Buchi, G.; Hansen, J. H.; Knutson, D.; Koller, E.
CORPORATE SOURCE: Massachusetts Inst. of Technol., Cambridge
SOURCE: J. Am. Chem. Soc. (1958), 80, 5517-24
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
AB The self-condensation of 3-methylcyclohex-2-en-1-one (I) in the presence of NaNH2 in boiling Et2O yielded II. Isophorone (III) and the 5-Me deriv. (IV) of I yield under identical conditions analogous dimeric compds. IV dimerizes by a rate-controlled process since on exposure to NaNH2 in boiling decane it is converted to V which is stabilized by intramol. H-bonding and which had previously been prepd. from IV and NaOH under drastic conditions (cf. Ayer and Taylor, C.A. 50, 5605g). Self-condensation of the 3-Ph analog (VI) of I yields VII which is the only one of the 9 mechanistically permissible structures stabilized by intramol. H-bonding. I, b23 90.5-1.5.degree., n26D 1.4921, (275 g.) in 500 cc. dry Et2O added during 1 hr. with stirring and cooling to 150 g. NaNH2 in 2 l. dry Et2O, stirred at room temp. overnight. poured into iced H2O, the aq. layer extd. with Et2O, and the combined Et2O solns. worked up yielded 87.5 g. I and 100 g. II, b12 210-22.degree., m. 73-4.degree. (Et2O-petr. ether); the distn. residue dissolved in hot C6H6 and cooled gave 16.3 g. leaflets, m. 186.degree., tentatively identified as a tetramer of I. II (0.4 g.) and 0.34 g. NaOAc refluxed a few min. in 3:1 EtOH-H2O, stored 2 days, concd., and cooled gave 0.35 monosemicarbazone of II, m. 210-12.degree. (decompn.) (Et2O); bis(2,4-dinitrophenylhydrazone) of II, yellow-orange needles, m. 263.degree. (decompn.) (C6H6), 78% yield. MeBr bubbled through 200 cc. Et2O contg. 3.10 g. Mg, the soln. heated to expel the excess MeBr, treated slowly with 6.05 g. II in 200 cc. dry Et2O, refluxed 18 hrs., and worked up gave 4.12 g. VIII, needles, m. 153.0-3.8.degree. (petr. ether). VIII (1.0 g.) and 1.89 g. powd. Se heated 9 hrs. at 300-20.degree., treated with an addnl. 0.6 g. Se, heated again 10 hrs., extd. with petr. ether, and the ext. chromatographed on Al2O3 gave 0.27 g. 1,3,5(or 7)-trimethyldibenzoselenophene (IX), which with picric acid gave the picrate, m. 120-1.degree. (Me2CO-EtOH); the picrate in hexane passed through Al2O3 gave free IX, needles, m. 86-7.degree. (Et2O-EtOH); IX gave an intense blue color in concd. H2SO4. VIII (1 g.) in 60 cc. C6H6 contg. 60 mg. iodine refluxed 4 hrs., the H2O removed azeotropically, and the crude product chromatographed from petr. ether on Al2O3 yielded X, b0.01 80.degree., n24D 1.5093; VIII could also be dehydrated with hot Ac2O. X (1 g.) and 1.6 g. powd. black Se heated 8 hrs. at 310-15.degree., treated with an addnl. 0.8 g. Se, heated 12 hrs., powd., extd. with Et2O in a Soxhlet app., the ext. evapd., and the residue chromatographed on Al2O3 yielded 0.08 g. IX. X (3.0 g.) and 2.0 g. S heated slowly during 2 hrs. from 220 to 250.degree., treated with 1 g. S, heated again 2 hrs., extd. with Me2CO in a Soxhlet app., the ext. evapd., the residue dissolved in 20 cc. C6H6 and 10 cc. EtOH, the soln. refluxed 5 hrs. with Raney Ni (from 20 g. alloy), the mixt. worked up, and the resulting brown oil (0.7 g.) chromatographed and distd. yielded 0.25 g. 2,4,3'-trimethylbiphenyl (XI). IX (0.16 g.) in 15 cc. C6H6 and 3 cc. C6H6

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refluxed 5 hrs. with 2.1 g. Raney Ni and the crude product chromatographed
yielded 0.09 g. XI, b3 108.degree., n24D 1.5731, which gave a deep yellow color with C(NO2)4. 2,4-Me2C6H3Br (30 g.) in 100 cc. dry Et2O treated with 3.9 g. Mg, the soln. treated slowly with 18 g. 3-methylcyclohexanone in 100 cc. Et2O, and the product isolated in the conventional manner yielded the following fractions: (1) 10.8 g. 1-[4-(m-xylyl)]-3-methyl-1-cyclohexene (XII), b5.5 121-2.degree., and (2) 7 g. 1-[4-(m-xylyl)]-3-methyl-1-cyclohexanol (XIII), b0.7 120.degree.. The iodine-catalyzed dehydration of XIII gave a good yield of XII. XII (12.8 g.) and 4.1 g. S heated 200 min. at 210-20.degree. and the product chromatographed on Al2O3
yielded XI, b3 107-8.degree., n25D 1.5732. II (4.4 g.) added with cooling
to 0.9 g. Na in 90 cc. abs. EtOH, cooled 1 hr., treated slowly with 2.72 g. iso-AmONO, kept overnight, poured into 350 cc. refluxing H2O, refluxed 1 hrs., cooled, washed with Et2O, and acidified to pH 2-3 with (CO2H)2 yielded 3.4 g. oximino ketone deriv. of II, m. 198-9.degree. (MeOH); the Et2O washings yielded 0.9 g. unchanged II. II (4.4 g.) added with cooling
to 1.8 g. Na in 140 cc. abs. EtOH, kept 1 hr. at 0.degree., treated slowly
with 5.45 g. iso-AmONO, kept overnight, poured into 550 cc. H2O, refluxed 1.5 hr., concd. to half the original vol., acidified to pH 2, refluxed 1 hr., extd. continuously with Et2O, and the ext. worked up yielded 2 g. bis(oximino ketone) deriv. of II, yellow prisms, m. above 350.degree. (MeOH). II (0.110 g.), 4 cc. EtOD, and 0.05 cc. 20% NaOD in D2O refluxed 15 min. under N, the solvent removed in vacuo, the residue treated with 4 cc. EtOD and 0.05 cc. D2O, the mixt. refluxed 15 min., the 2nd step repeated twice, the final residue treated with 3 cc. D2O and extd. with 15
cc. Et2O, the ext. washed with 2 cc. D2O, dried, and distd. yielded 0.085 g. II contg. 5.82 D atoms/mol., m. 71-2.degree. (Et2O-petr. ether). II (43 g.), 3 g. PtO2, and 500 cc. EtOH hydrogenated 45 min. at 29 lb. yielded 19 g. ketol, C14H22O2 (XIV), m. 100-2.degree. (EtOH). XIV (19 g.), 12.7 g. phthalic anhydride, 13.7 g. pyridine, and 50 cc. C6H6 refluxed 3 hrs., poured into 100 cc. iced H2O, extd. with C6H6, and the ext. worked up yielded 85% H phthalate (XV) of XIV, m. 187-8.5.degree. (C6H6-hexane). XV (27 g.) in 250 cc. Me2CO added to 34 g. brucine in 500 cc. Me2CO, refrigerated 2 hrs., concd. to 400 cc., and stored overnight yielded 13.6 g. brucine salt (XVI) of XV, m. 195-204.degree.; 9 g. 2nd crop. XVI (3 g.) treated with 100 cc. 10% HCl, extd. with C6H6, and the ext. worked up gave 1.5 g. (+)-XV, m. 160-4.degree. (C6H6-hexane), [.alpha.]25D 30.6.degree. (c 1.82, CHCl3) (29.5.degree. and 29.6.degree. in 2 other prepns.). (+)-XV (2.7 g.) refluxed 6 hrs. with 50 cc. 15% aq. NaOH and the product isolated with Et2O yielded (+)-XIV, noncrystg. viscous oil. (+)-XIV (2.5 g.) in 30 cc. pyridine added with cooling to 3.0 g. CrO3 in 35 cc. pyridine, kept at room temp. overnight, extd. with Et2O, the ext. distd., and the crude product (1.9 g.) chromatographed on Al2O3 yielded 0.9 g. (-)-II, m. 58-62.degree., .alpha. -1.04.degree. (0.4023 g. in 1.5 cc. CHCl3). (-)-II (0.9 g.), 2.5 cc. 95% N2H4, 1.2 g. Na, and 50 cc. (HOCH2CH2)2O heated 4 hrs. at 140-50.degree., treated with an addnl. 1 cc. N2H4, heated 14 hrs. at 210-15.degree., dild. with H2O, extd. with petr. ether, and the ext. chromatographed on 20 g. Al2O3 yielded 0.387 g. XVII, b0.4 about 70.degree., .alpha. -0.003 (0.3058 g. in

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1.5 cc. CHCl3). II (0.48 g.) reduced in the same manner yielded 0.317 g. dl-XVII, b0.2 70.degree., n23D 1.4988. IV (11.0 g.), b8 81-2.5.degree., treated in the usual manner with 6.0 g. NaNH2 yielded 4.91 g. crude product which chromatographed on Al2O3 gave 2.25 g. XVIIIa, m. 110-10.5.degree., and 2.52 g. XVIIIb, m. 114-14.5.degree., which gave isomeric 2,4-dinitrophenylhydrazones m. 192-6.degree., and 201-3.5.degree., resp.; the distn. residue chromatographed on Al2O3 yielded less than 4% V, m. 115-17.degree.. XVIIIa and XVIIIb deuteriated in the usual manner showed replacement of 6 D atoms/mol. XVIIIb (500 mg.)
and 500 mg. NaNH2 in 15 cc. decane refluxed 45 min., the mixt. worked up, the crude product sepd. with NaOH into phenolic and neutral parts, and the
phenolic portion (260 mg.) chromatographed on silica gel yielded 67 mg. 3,5-Me2C6H3OH (XIX), m. 116-19.degree.. IV (3.0 g.) added during 15 min. dropwise to 3.5 g. NaNH2 in 80 cc. p-cymene, refluxed 0.5 hr., poured into
350 cc. iced H2O, extd. with C6H6, and the ext. worked up yielded 2.19 g. XIX, m. 64-4.5.degree.; 3,5-dinitrobenzoate m. 193.5-94.degree.. IV (5.0 g.), 3.4 g. NaNH2, and 100 cc. dry decane refluxed 0.5 hr., poured into 200 cc. iced H2O, the aq. layer acidified with concd. HCl to yield 3.0 g. XIX, and the hexane layer chromatographed on Al2O3 yielded 0.93 g. V, m. 106-10.degree. (aq. EtOH) [2,4-dinitrophenylhydrazone m. 184-6.degree.], and 0.19 g. XVIIIb, m. 112-13.degree. (Et2O-petr. ether). III (20 g.) in 150 cc. Et2O added with stirring to 8.4 g. NaNH2 in 200 cc. abs. Et2O, refluxed 5 hrs., cooled, poured onto ice, extd. with Et2O, and the ext. worked up gave 13 g. unchanged III and 3 g. viscous oily, b0.6 117-19.degree., which chromatographed on Al2O3 gave XX, m. 121-2.degree. (Et2O-petr. ether). Deuteriation of XX yielded 87% material contg. 6 atoms D/mol. VI (4.75 g.), 1.8 g. NaNH2, and 30 cc. Et2O refluxed 19 hrs., poured into 100 cc. iced H2O, extd. with Et2O, the ext. evapd., and the residue chromatographed on Al2O3 yielded 3.38 g. unchanged VI and 0.10
g. VII, m. 190-2.degree. (EtOAc).

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ACCESSION NUMBER:	1958:55682 CAPLUS
DOCUMENT NUMBER:	52:55682
ORIGINAL REFERENCE NO.:	52:9970b-i,9971a-b
TITLE:	Stereochemistry of ketonization. IV
AUTHOR(S):	Zimmerman, Howard E.
CORPORATE SOURCE:	Northwestern Univ., Evanston, IL
SOURCE:	J. Am. Chem. Soc. (1957), 79, 6554-8
DOCUMENT TYPE:	Journal
LANGUAGE:	Unavailable

AB cf. C.A. 51,5715f. The irreversible ketonization of the enol of 1-acetyl-2-phenylcyclohexane (I) yielded predominantly the cis isomer of I. The degree of selectivity is rationalized with a concept of specific and nonspecific steric hindrance. CuCl (0.20 g.) and 0.12 mole PhMgBr in 45 cc. Et2O refluxed 10 min., treated dropwise during 20 min. with 5.0 g. 1-acetylcyclohexene (Ia), n25D 1.4920, in 30 cc. dry Et2O, refluxed 45 min., poured onto 200 g. ice and 200 cc. satd. aq. NH4Cl, extd. with hexane, the ext. evapd., and the residual reddish oil chromatographed on silica gel gave 2.18 g. cis-I contaminated with small amts. of Ph2, 1.20 g. pure cis-I, m. 41.0-1.5.degree. (MeOH) (semicarbazone, m. 185-6.5.degree.), 0.26 g. pure trans-I, m. 79-80.degree., and 0.29 g. trans-I contaminated with a hydroxylic impurity. PhCH:CHAc (100 g.) treated at 200.degree. with stirring with a slow stream of (CH2:CH)2 during 12 hrs. and the mixt. distd. yielded 68.47 g. (crude) trans-1-acetyl-2-phenyl-4-cyclohexene (II), m. 59-61.degree. (hexane). II
(9.10 g.) in 75 cc. EtOAc hydrogenated over 50 mg. PtO2 yielded 7.93 g. trans-I, m. 79.5-81.5.degree.; semicarbazone, m. 183-6.degree.. PhCH:CHCH:CH2 (27 g.), 18 g. CH2:CHAc, 20 cc. C6H6, and 10 mg. hydroquinone refluxed 6 hrs. under N and distd. yielded 30.34 g. mixt. of cis- and trans-1-acetyl-2-phenyl-3-cyclohexene (III), b0.10 105-10.degree., n25D 1.5479-1.5493, contg. 80% cis-III. cis-trans-III (30.34 g.) in 100 cc. EtOAc hydrogenated over 245 mg. PtO2, filtered, evapd., and a 10-g. portion of the residue chromatographed on silica gel yielded 7.88 g. cis-I and 1.87 g. trans-I. cis-I (202 mg.) in 10 cc. AcOH
treated during 7 min. with 176 mg. Br, dild. with 100 cc. H2O, extd. with 1:1 Et2O-pentane, the ext. worked up, and the residue recrystd. from hexane yielded 128 mg. 1-Br deriv. (IV) of I, m. 93-4.degree.. cis-I (6.18 g.) in 100 cc. AcOH treated with 5.12 g. Br, worked up after 15 min., and the resulting product (8.51 g.) crystd. from 60 cc. hot hexane yielded 4.74 g.IV. CuCl (0.25 g.) and PhMgBr from 22.0 g. PhBr and 3.40 g. Mg in 50 cc. Et2O refluxed 15 min., treated during 25 min. with 14.0 g.
Ia in 20 cc. dry Et2O, refluxed 1.5 hrs., cooled, treated with 22.4 g. Br,
cooled 15 min., dild. with H2O and ice, extd. with Et2O, the ext. worked up, and the product chromatographed on silica gel yielded 7.62 g. IV and 3.16 g. trans-I. trans-I (3.00 g.) in 100 cc. AcOH treated with 2.40 g. Br during 3 hrs., dild. with 500 cc. H2O, extd. with Et2O, and the oily residue from the ext. chromatographed on silica gel yielded 0.47 g. trans-1-dibromoacetyl-2-phenylcyclohexane (V), m. 97.0-7.5.degree. (hexane), and 0.62 g. trans-1-bromoacetyl-2-phenylcyclohexane (VI), m. 59.5-60.5.degree. (hexane). VI (56.0 mg.) in 1.0 cc. Me2CO treated 1.5 min. with 0.10 cc. 47% HI, poured into 10 cc. aq. Na2S2O3, and filtered yielded pure trans-I. VI (168 mg.) in 5.0 cc. Me2CO treated 2.5 min. with
0.50 cc. 47% HI, dild. with 30 cc. aq. Na2S2O3, and worked up gave 120.2 g. trans-I. V (56 mg.) in 1.0 cc. Me2CO treated 1.5 min. with 0.10 cc. 47% HI in 1.0 cc. Me2CO gave a mixt. of VI and trans-I which in 2.0 cc. Me2CO with 0.15 cc. HI gave trans-I contaminated with some cis-I. cis-I

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(50 mg.) and 0.10 cc. 47% HI in 2.0 cc. Me2CO kept 5 min. at room temp. and poured into H2O gave unchanged cis-I. trans-I (404 mg.) and 0.20 cc. HBr in 15 cc. AcOH refluxed 1.75 hrs., dild. with H2O, extd. with Et2O-hexane, the ext. worked up, and the residual oil treated with 3.0 cc.
47% HI in 30 cc. Me2CO gave only trans-I. IV (56.0 mg.) in 2.0 cc. Me2CO treated 1.5 min. with 0.10 cc. 47% HI, poured into 15 cc. aq. Na2S2O3, and
extd. with Et2O gave 46.3 mg. 91.2%-pure cis-I. IV (56.0 mg.) in 5.0 cc. Et2O reduced with 300 mg. Zn dust and 1.0 cc. AcOH during 14 hrs. yielded 89.4% cis-I. A similar run with 56.0 mg. IV and 300 mg. Zn dust in 5.0 cc. MeOH in the presence of 300 mg. collidine-HCl (VII) gave during 17 hrs. 92.4% cis-I; the yield was 92.3% when 10 cc. MeOH was used. IV (56.0
mg.), 10 cc. MeOH, and 300 mg. each of glycine and Zn dust yielded 91.3% cis-I. IV (56.0 mg.), 10 cc. MeOH, and 300 mg. each of NH4Cl and Zn dust heated 17 hrs. under N gave 93.8% cis-I. IV (56.0 mg.), 10 cc. Me3COH, and 300 mg. each of VII and Zn dust gave during 28, 20, and 22 hrs. 91.2, 90.8, and 90.5%, resp., cis-I. A similar run in 10 cc. C6H6 under N yielded during 24 hrs. 88.8% cis-I. IV (56.0 mg.), 10 cc. MeCN, and 300 mg. each of Zn dust and VII yielded during 22 hrs. under N 93.6% cis-I. IV (112 mg.) debrominated with Zn in C6H6 in the presence of VII in the absence of N yielded 79 mg. crude 1-HO deriv. of I, m. 86.0-7.5.degree. (hexane). cis-I (100 mg.) added to 40 mg. Na and 5.0 cc. EtOH kept 8 hrs.
at room temp., dild. with 40 cc. H2O, and filtered yielded 100.3 mg. mixed
isomeric I, m. 77-9.degree., contg. 13.1% cis-I.

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ACCESSION NUMBER: 1958:55681 CAPLUS
DOCUMENT NUMBER: 52:55681
ORIGINAL REFERENCE NO.: 52:9970a-b
TITLE: Magnesium in ester condensations
AUTHOR(S): Laukkanen, I. L. Pentti
CORPORATE SOURCE: Univ. Helsinki
SOURCE: Suomen Kemistilehti (1957), 30B, 139-42
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
AB Diethyl adipate was condensed to 2-carbethoxycyclopentanone with Mg(OEt)2 by 2 routes, one EtO group reacting in one, and both reacting in the other. The molar quantity of Mg(OEt)2 used for the first reaction was twice that used in the second.

L33 ANSWER 10 OF 18 CAPLUS COPYRIGHT 2001 ACS
ACCESSION NUMBER: 1958:25576 CAPLUS
DOCUMENT NUMBER: 52:25576
ORIGINAL REFERENCE NO.: 52:4653f-i,4654a-i
TITLE: Pyridazines. II. Preparation of pyridazines from furan derivatives
AUTHOR(S): Levisalles, Jacques
CORPORATE SOURCE: Ecole polytech., Paris
SOURCE: Bull. soc. chim. France (1957) 997-1003
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
AB cf. C.A. 51, 12924e. Oxidation of furans, 2,3,4,5-RR'R''R'''C4O (I), by Br in the presence of MeOH gave a series of 2,5-dimethoxy-2,5-dihydrofurans, 2,5-(MeO)2-2,3,4,5-RR'R''R'''C4O (II), converted by refluxing in 1% AcOH with N2H4.H2O to the corresponding pyridazines, 3,4,5,6-RR'R''R'''C4N2 (III). M.ps. were uncor. and the ultraviolet absorption measurements were made in CHCl3. Na2CO3 (120 g.) and 26 g. 2-EtC4H3O in 1 l. MeOH treated at -5 to 2.degree. with 13.5 cc. Br in 200 cc. MeOH, the mixt. dild. with 1.5 l. satd. aq. NaCl, extd. 3 times with 250 cc. C6H6, the combined dried exts. evapd., and the residue distd. gave 43 g. II (R = Et, R' = R'' = R''' = H) (V), b13 63.degree., n20D 1.4364. V(7.9 g.) reduced with Pd-SrCO3 in MeOH yielded 71% of the corresponding 2,5-dimethoxytetrahydrofuran, 2,5-(MeO)2-2,3,4,5-RR'R''R'''C4H2O (VI, R = Et, R' = R'' = R''' = H), b20 69.degree., n18D 1.4302, characterized by the bis(dinitrophenylhydrazone) of 4-oxohexanal, m. 176.degree., .lambda. 357 m.mu. (.epsilon. 39,500). Similarly, 22 g. 2-PrC4H3O and 80 g. Na2CO3 in 750 cc. MeOH oxidized at -6 to -2.degree. with 10 cc. Br in 150 cc. MeOH gave 30.7 g. II (R = Pr, R' = R'' = R''' = H), b18 76-8.degree., n20D 1.4402, reduced to 69% VI (R = Pr, R' = R'' = R''' = H), b20 93.degree., n20D 1.4287; bis(dinitrophenylhydrazone) of 4-oxoheptanol, m. 174-5.degree., .lambda. 358 m.mu. (.epsilon. 42,300). Oxidation of 27.5 g. 2-BuC4H3O at -25.degree. gave 29 g. II (R = Bu, R' = R'' = R''' = H), b15 91-100.degree., n21D 1.4387. Similarly were prepd. in 60 and 51.7% yields the corresponding II (R = R''' = Me, R', = R'' = H) (VII), b16 59.degree., n16D 1.4312, and II (R = Me, R''' = Pr, R' = R'' = H), b22 87-9.degree., n21D 1.4535. V (7.9 g.) in 15 cc. 1% AcOH and 4 cc. MeOH refluxed 10 min., the cooled soln. treated with 2.6 cc. N2H4.H2O, the mixt. refluxed 1 hr., extd. with CHCl3, and the ext. dried and distd. in vacuo gave 2.5 g. III (R = Et, R' = R'' = R''' = H), b14 103-4.degree., n18D 1.5053, .lambda. 255, 324 m.mu. (.epsilon. 1180, 294); picrate, m. 135.degree. (MeOH). Similarly were prepd. the corresponding III (substituents, b.p., % yield, n, .lambda. in m.mu. (.epsilon.), and m.p. of the picrolonate given): R = Pr, R' = R'' = R''' = H, b13 108-9.degree., 44.2, n17D 1.4978, 255, 322 (1240, 271), 123-5.degree. (decompn.); R = Bu, R' = R'' = R''' = H, b25, 134.degree., 49, n22D 1.4937, - (-), 134-5.degree.; R = R''' = Me, R' = R'' = H, -, 71, -, - (-) [picrate, m. 167.degree., 258, 267, 309 (1815, 1200, 330)]; R = Me, R''' = Pr, R' = R'' = H, b16 124.degree., 27.2, n20D 1.5015, - (-), 147.degree. (decompn.). VII (15.8 g.) and 20 cc. 1% AcOH refluxed 10 min., the cooled mixt. neutralized with 50 cc. 2% Na2CO3, satd. with aq. NaCl, extd. with CHCl3,

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and the ext. dried and distd. in vacuo gave 8.1 g. cis-(:CHAc)2 (VIII), b16 92.degree., n16D 1.4571, .lambda. 223, 282 m.mu. (.epsilon. 6000, 175); bis(dinitrophenylhydrazone), m. 276-8.degree., .lambda. 407.5 m.mu. (.epsilon. 46,000). I (R = R''' = Me, R' = R'' = H) (43 cc.) and 80 g. anhyd. KOAc in 520 cc. MeOH treated at -7.degree. with 20 cc. Br in 250 cc. MeOH, the mixt. kept 2 hrs., poured into 1 l. satd. aq. NaCl, neutralized immediately with satd. aq. Na2CO3, filtered, the filtrate extd. with CHCl3, and the product recrystd. from C6H12 in the presence of animal C gave 18.6 g. trans isomer (IX) of VIII, m. 76-7.degree. (after sublimation), .lambda. 228, 324 m.mu. (.epsilon. 14,600, 70), also prepd. by addn. of a drop of concd. HBr to 0.5 g. VIII in 2 cc. MeOH and by treating 3.95 g. VII with 0.3 cc. concd. HCl, taking up the solid mass in CHCl3, stirring with satd. NaHCO3 soln., evapg. the dried ext., and purifying the product by pressing on a porous plate. IX (1.1 g.) and 2.05 g. (CH:CHPh)2 heated, the melt kept 5 min. at 100.degree. and 1 min. at 180.degree., the cooled mixt. taken up in 10 cc. C6H6, and the product (2.15 g.) recrystd. from C6H12 gave trans-3,6-diphenyl-1,2-diacetyl-4-cyclohexene (X), m. 138.degree., .lambda. 258 m.mu. (.epsilon. 2800), .nu. 1968 cm.-1 (CO) (Nujol). IX condensed according to Schenck (C.A. 44, 557e) with (CH:CH2)2 by heating 12 hrs. at 100.degree. in a sealed tube gave trans-1,2-diacetyl-4-cyclohexene (XI), b13 118.degree., n22.5D 1.4799, .nu. 1706, 1657 cm.-1; (p-nitrophenyl)pyrrole, m. 113.5.degree., .lambda. 337 m.mu. (.epsilon. 6800); bis-(dinitrophenylhydrazone), m. 210.degree. (decompn.), .lambda. 361 m.mu. (.epsilon. 42,600). XI hydrogenated with Pd-SrCO3 gave the corresponding trans-1,2-diacetylcyclohexane, b155 115.degree., n22.5D 1.4680; (p-nitrophenyl)pyrrole, m. 113.degree., .lambda. 340 m.mu. (.epsilon. 7100); bis(dinitrophenylhydrazone), m. 200.degree. (decompn.), .lambda. 365 m.mu. (.epsilon. 43,200). VII (8.1 g.) treated with 17 cc. (CH:CH2)2 and 40 cc. Et2O at -10.degree., autoclaved 14 hrs. at 130.degree., and the cooled mixt. evapd. gave 5.5 g. cis-1,2-diacetyl-4-cyclohexene (XII), b15 131-2.degree., m. 52.degree. n18D 1.4875, .nu. 1704, 1656 cm.-1; bis(dinitrophenylhydrazone), m. 218.degree. (decompn.), .lambda. 358 m.mu. (.epsilon. 40,600). XII (5.5 g.) hydrogenated with Pd gave 4.1 g. cis-1,2-diacetylcyclohexane, b18 130.degree., n25D 1.4678, .nu. 1698 cm.-1; bis(dinitrophenylhydrazone), m. 204-5.degree., .lambda. 357 m.mu. (.epsilon. 40,250). XI (24.1 g.) reduced with Pd-SrCO3, the mixt. filtered, the solvent evapd., the residue distd. in the presence of 4 drops of concd. H2SO4, the distillate collected on anhyd. K2CO3, the mass extd. with Et2O, the ext. evapd., and the residue distd. gave 13.0 g. 4,5,6,7-tetrahydro-1,3-dimethylbenzo[c]furan, b16 90-8.degree., n20D 1.4912, also obtained by similar treatment of XII (cf. Morel and Verkade, C.A. 45, 7562d). IX (2.25 g.) and 3 cc. CH2:CHCMe:CH2 in 12 cc. C6H6 refluxed 8 hrs. with addn. of 2 cc. diene after 2 and 8 hrs., the mixt. kept overnight, evapd., the residue distd. at 135.degree./18 mm., and the product redistd. gave 2.5 g. trans-4-methyl-1,2-diacetyl-4-cyclohexene, b16 125.degree., n20D 1.4791, .lambda. 273 m.mu. (.epsilon. 340), .nu. 1701, 1646 cm.-1; (p-nitrophenyl)pyrrole, m. 157.degree. (decompn.), .lambda. 338 m.mu. (.epsilon. 7100); bis(dinitrophenylhydrazone) m. 177-9.degree. (C5H5N-EtOH), .lambda. 361 m.mu. (.epsilon. 41,900). Hydrogenation of the unsatd. adduct (3.6 g.) gave 2.5 g. trans-4-methyl-1,2-diacetylcyclohexane, b14 122-3.degree., n19D 1.4633, .nu. 1705 cm.-1; (p-nitrophenyl)pyrrole, m. 143.degree., .lambda. 340 m.mu. (.epsilon. 7100); bis(dinitrophenylhydrazone), m. 186-8.degree. (C5H5N-EtOH), .lambda. 363 m.mu. (.epsilon. 42,400). IX (5.6 g.), 10 cc.

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(CHMe:CH2)2, and 25 cc. C6H6 refluxed 9 hrs., the mixt. kept overnight, the solvent evapd., and the residue distd. in vacuo gave 8.5 g. trans-4,5-dimethyl-1,2-diacetyl-4-cyclohexene, b1.0 100.degree., m. 36-7.degree., .nu. 1710, 1655 cm.-1; (p-nitrophenyl)pyrrole, m. 193.degree. (C6H12), .lambda. 340 m.mu. (.epsilon. 7300); bis(dinitrophenylhydrazone), m. 227.degree., .lambda. 361 m.mu. (.epsilon. 40,360). Hydrogenation of 1.95 g. of the unsatd. adduct gave trans-4,5-dimethyl-1,2-diacetylcyclohexane, b16 133.degree., n20D 1.4650, .nu. 1705 cm.-1; (p-nitrophenyl)pyrrole, m. 168.degree., .lambda. 340 m.mu. (.epsilon. 7600); bis(dinitrophenylhydrazone), m. 214-15.degree., .lambda. 363 m.mu. (.epsilon. 43,400).

L33 ANSWER 11 OF 18 CAPLUS COPYRIGHT 2001 ACS
ACCESSION NUMBER: 1958:25575 CAPLUS
DOCUMENT NUMBER: 52:25575
ORIGINAL REFERENCE NO.: 52:4653c-f
TITLE: Pyridazine quaternary salts
AUTHOR(S): Blood, A. E.; Noller, C. R.
CORPORATE SOURCE: Stanford Univ., Stanford, CA
SOURCE: J. Org. Chem. (1957), 22, 844-5
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
AB Pyridazine (I) (5.5 g.) in 20 cc. CCl4 added dropwise with cooling and stirring to 25.6 g. cis-(BrCH2CH:)2 in 35 cc. CCl4, the mixt. kept 4 hrs. at 0.degree., the CCl4 decanted, and the residue crystd. from PrOH gave 9.7 g. gray trans-1,4-dipyridazinium-2-butene dibromide (II), m. 179-80.degree. (decompn.), .lambda. 6.32, 7.05, 8.41, 9.16, 9.91, 10.0, 12.56 .mu. (Nujol) (lack of band near 6 .mu. indicated that the double bond was trans and symmetrically substituted). II was similarly obtained from mixts. in CCl4 at reflux temp. and in Me2CO at room temp. There was no evidence for the formation of the cis-isomer, of 1-(4-bromo-2-buten-1-yl)pyridazinimn bromide, of 1,2-bis(4-bromo-2-buten-1-yl)-pyridazinium dibromide, of 9,10-diaza-1,4-dihydronaphthalene dibromide, or of products that might have resulted from allylic rearrangement of (:CHCH2Br)2 before or during the reaction with I. Equally unsuccessful were attempts to prep. simpler diquaternary salts. I (5.5 g.) and 34 g. MeI heated 12 hrs. at 100.degree. in a sealed tube and the mixt. added to 40 cc. Me2CO at 0.degree. gave 11.3 g. 1-methylpyridazinium iodide, m. 95-6.degree. (decompn.) (PrOH), .lambda. 6.30, 6.88, 10.18, 12.84 .mu.. The same product was obtained in the absence of solvent at 0.degree. and in MeOH at 110.degree.. I (2.21 g.) and 14.5 g. EtBr heated 20 hrs. in a sealed tube at 110.degree., the chilled mixt. filtered in a dry box, and the residue washed with Me2CO and crystd. from PrOH gave the very hygroscopic 1-ethylpyridazinium bromide, m. 118-20.degree. (decompn.), .lambda. 6.30, 8.44, 10.08, 12.84 .mu. (Nujol).

L33 ANSWER 12 OF 18 CAPLUS COPYRIGHT 2001 ACS
ACCESSION NUMBER: 1957:81123 CAPLUS
DOCUMENT NUMBER: 51:81123
ORIGINAL REFERENCE NO.: 51:14572c-d
TITLE: Preparation of hydroaromatic compounds on the basis of products of the diene synthesis. IV. Reaction of organo-magnesium compounds with esters of 4-cyclohexenedicarboxylic acids
AUTHOR(S): Sopov, N. P.
SOURCE: J. Gen. Chem. U.S.S.R. (1956), 26, 1795-1801
DOCUMENT TYPE: Journal
LANGUAGE: English
AB See C.A. 51, 1868i.

L33 ANSWER 13 OF 18 CAPLUS COPYRIGHT 2001 ACS
ACCESSION NUMBER: 1957:81122 CAPLUS
DOCUMENT NUMBER: 51:81122
ORIGINAL REFERENCE NO.: 51:14572e
TITLE: Structure of thujone tribromide
AUTHOR(S): Iloff, Phillip M., Jr.
CORPORATE SOURCE: Stanford Univ., Stanford, CA
SOURCE: (1957) 99 pp.;microfilm, $2.00; paper enlargement, $9.90 Avail.: Univ. Microfilms (Ann Arbor, Mich.), Order No. 21571
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DOCUMENT TYPE: Dissertation
LANGUAGE: Unavailable
AB Unavailable

L33 ANSWER 14 OF 18 CAPLUS COPYRIGHT 2001 ACS
ACCESSION NUMBER: 1957:81121 CAPLUS
DOCUMENT NUMBER: 51:81121
ORIGINAL REFERENCE NO.: 51:14572b-c
TITLE: Synthesis of 4-isopropyl-1-methylbicyclo[3,1,0]-3-hexen-2-one
AUTHOR(S): Smith, Howard E.
CORPORATE SOURCE: Stanford Univ., Stanford, CA
SOURCE: (1957) 97 pp.;microfilm, $2.00; paper enlargement, $9.70 Avail.: Univ. Microfilms (Ann Arbor, Mich.), Order No. 20467
From: Dissertation Abstr. 17, 1470-1
DOCUMENT TYPE: Dissertation
LANGUAGE: Unavailable
AB Unavailable

L33 ANSWER 15 OF 18 CAPLUS COPYRIGHT 2001 ACS
ACCESSION NUMBER: 1957:66547 CAPLUS
DOCUMENT NUMBER: 51:66547
ORIGINAL REFERENCE NO.: 51:**12049f-i,12050a-d**
TITLE: Diene syntheses with 1-diethylaminobutadiene and thermal cleavage of the adducts
AUTHOR(S): Hunig, Siegfried; Kahanek, Herbert
CORPORATE SOURCE: Univ. Marburg, Germany
SOURCE: Chem. Ber. (1957), 90, 238-45
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

AB cf. preceding abstr. Adding (20 min.) 105 g. freshly distd. MeCH:CHCHO in 150 cc. C6H6 to 225 g. Et2NH and 60 g. anhyd. K2CO3 at -10 to -5.degree., keeping the mixt. 1 hr. at 0.degree. and 4 hrs. at 20.degree., decanting it from the K2CO3, adding 0.9 g. phenanthrene quinone, and distg. it in vacuo yield 123 g. crude or 114 g. pure 1-diethylaminobutadiene (I), b1064-6.degree.. I reacts with AcOH exothermically with the formation of a black resin; this reaction is used as a test for the completion of the following reactions. Treating 31 g. I in 60 cc. C6H6 with 35 cc. freshly distd. CH2:CHCO2Et 6 days in the dark, adding 50 cc. Et2O, extg. with 200 + 50 cc. 2N HCl, making the acid soln. alk., and extg. with Et2O yield 94% Et cis-2-diethylamino-.DELTA.3-tetrahydrobenzoate (II), b0.2 80-3.degree., which, refluxed with 20% HCl, yields .DELTA.1,3-dihydrobenzoic acid (dibromide, m. 167-9.degree.). Hydrogenating 33.8 g. II in 200 cc. EtOH with 0.5 g. PtO2, evapg. the filtered soln. in vacuo, taking up the residue with Et2O and 2N HCl, and making the acid soln. alk. give 76% Et cis-2-diethylaminohexahydrobenzoate, b11 124-5.degree.; it gives the expected methiodide; the free acid, on heating with concd. HCl, rearranges to the trans acid. Adding 12.4 g. II in 30 cc. abs. Et2O dropwise to 2 g. LiAlH4 in 100 cc. Et2O at 0.degree., keeping the mixt. 0.5 hr. at 0.degree., refluxing it 0.5 hr., then adding dropwise 1.5 cc. 20% Na2CO3 + 11 cc. H2O at 0.degree., and distg. the residue of the Et2O give 95.5% cis-2-diethylamino-.DELTA.3-tetrahydrobenzyl alc., b11 125-7.degree. (picrate, m. 102.degree.). Treating 45 g. I in 50 cc. C6H6 with 27 g. CH2: CHCN at 20-30.degree., keeping the mixt. 2 days, and distg. it yield 93% 2-diethylamino-.DELTA.3-tetrahydrobenzonitrile, b11 125-6.degree., which, hydrogenated 3 hrs. in MeOH with PtO2, yields 81% 2-diethylaminohexahydrobenzonitrile (III), b12 130-2.degree. (picrate, m. 119-20.degree.). Refluxing 18 g. III in 80 cc. 20% HCl 3 days, washing the soln. with Et2O, making it alk., washing it again with Et2O, acidifying again with HCl, evapg. to dryness, extg. the residue with boiling EtOH, neutralizing the HCl with NaOEt, and distg. the residue of the filtered soln. yield 58% trans-2-diethylaminohexahydrobenzoic acid, b0.08 129-36.degree., needles contg. H2O, m. 62-4.degree., m. 90-2.degree. (H2O-free). Adding dropwise 90 g. MeCOCH:CH2 in 120 cc. C6H6 to 102 g. I in 100 cc. C6H6, keeping the mixt. 1 day at 0.degree., extg. with HCl, adding Et2O to the aq. layer, making it alk., and evapg. the Et2O yield 42% 2-diethylamino-.DELTA.3-tetrahydroacetophenone, yellow oil, b0.2 86-7.degree. (semicarbazone, m. 160-3.degree.). Evapn. of the C6H6 soln. gives .DELTA.1,3-dihydroacetophenone (IV), b12 79-81.degree., which,

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heated with concd. H2SO4, yields PhAc. Heating 6.1 g. IV and 4.9 g. maleic anhydride until a reaction sets in, then heating it another 5 min. yield 77% diene adduct (V), m. 121.degree.. Carefully adding 26 g. CH2:CHCHO in 50 cc. Et2O to 51.5 g. I in 50 cc. abs. Et2O at -5.degree., keeping the mixt. 5 hrs. at 0.degree., making the soln. up to 200 cc. with Et2O, and distg. 50 cc. yield 84% cis-2-diethylamino-.DELTA.3-tetrahydrobenzaldehyde (VI), b0.6 77-8.degree.; treating another 100 cc. with 25 g. H2NOH.HCl in 75 cc. H2O at -5.degree., stirring the mixt. 1 hr., adding 50 cc. H2O, and making the aq. layer alk. with 12 g. KOH in 50 cc. H2O give 88% oxime of VI, m. 85-6.degree.. Adding the remaining 50 cc. to 3.8 g. LiAlH4 in 100 cc. Et2O at 0.degree. with stirring yields 92% cis-2-diethylamino-.DELTA.3-tetrahydrobenzyl alc., b10 122-3.degree. (picrate, m. 101.5.degree.). The thermal cleavage of Et2NH from these adducts occurs monomolecularly and is accelerated according to the substituents in the order CHO < COMe < CO2R .mchgt. CN.

L33 ANSWER 16 OF 18 CAPLUS COPYRIGHT 2001 ACS
ACCESSION NUMBER: 1957:66546 CAPLUS
DOCUMENT NUMBER: 51:66546
ORIGINAL REFERENCE NO.: 51:**12049b-f**
TITLE: The stereoisomeric N-ethylated hexahydroanthranilic acids
AUTHOR(S): Hunig, Siegfried; Kahanek, Herbert
CORPORATE SOURCE: Univ. Marburg, Germany
SOURCE: Chem. Ber. (1957), 90, 234-8
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

AB cf. following abstr. Refluxing 13.7 g. Et trans-hexahydroanthranilate, 30 g. Et2SO4, 16 g. pptd. CaCO3, and 80 cc. PhCl 8 hrs., extg. the soln. with dil. HCl, making the aq. soln. alk., and extg. with Et2O give 78% Et trans-N-ethylhexahydroanthranilate (I), bu11 111-13.degree.. Refluxing 4.5 g. cis isomer of I in 30 cc. 20% HCl 5 hrs. and evapg. the soln. in vacuo yield 80% cis-N-ethylhexahydroanthranilic acid (II).HCl, m. 205-6.degree.; free II, m. 175-6.degree.. Heating 0.5 g. II.HCl in 5 cc. concd. HCl 10 hrs. at 180-90.degree., dilg. the mixt. with H2O, washing the soln. with Et2O, evapg. the aq. soln., and treating the residue with Ag2CO3 give the trans acid, m. 227-9.degree., which, m. 231-2.degree., is also obtained on sapon. of I. Heating 4.3 g. II with 15 g. Et2SO4 7 hrs. at 130-40.degree., extg. the mixt. with dil. HCl, washing the aq. soln. with Et2O, making it alk., and extg. with Et2O yield 73% Et cis-N-diethylhexahydroanthranilate (III), b12 124-5.degree., which (0.5 g.), heated with 0.7 g. MeI in 10 cc. C6H6 1 hr. in a sealed tube on a water bath, gives III methiodide, leaflets, m. 157.5.degree.. Trans isomer (IV) of III, b12 124-5.degree., prepd. similarly, gives an oily methiodide. Refluxing 3.5 g. IV in 10 cc. 20% HCl 6 hrs., dilg. the soln. with H2O, treating it with Ag2CO3, evapg. the filtered soln. in vacuo, and recrystg. the residue from moist EtOAc give 72% trans-N-diethylhexahydroanthranilic acid (V), needles contg. H2O, m. 62-4.degree., m. 92-3.degree. (H2O-free); cis isomer of V is a hygroscopic sirup which, (1 g.) heated with 10 cc. concd. HCl 10 hrs. at 150-60.degree. and the residue of the evapd. soln. treated with Ag2CO3, gives V. Heating III or IV in PhCH2OH at 155.degree., passing the Et2NH split off into H2O by means of an N stream, and titrating it show that III splits off Et2NH 3.2 times faster than does IV.

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ACCESSION NUMBER: 1957:9170 CAPLUS
DOCUMENT NUMBER: 51:9170
ORIGINAL REFERENCE NO.: 51:**18681,1869a-h**
TITLE: Preparation of hydroaromatic compounds on the basis of products of the diene synthesis. IV. Action of organomagnesium compounds to esters of 4-cyclohexenedicarboxylic acids
AUTHOR(S): Sopov, N. P.
CORPORATE SOURCE: Inst. Aviation Instr., Leningrad
SOURCE: Zhur. Obshchei Khim. (1956), 26, 1602-9
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

AB cf. C.A. 50; 3292c. Condensation of dienes with esters of unsatd. acids by a previously described method (cf. Petrov and Sopov, C.A. 49, 5329h) yielded the following esters used as starting materials (b.p., d20, and nD20 given): cis-di-Me 4-cyclohexene-1,2-dicarboxylate (I), b20 141.5-2.degree., 1.1448, 1.4729; trans isomer (II), b20 139-9.5.degree., 1.1269, 1.4680; cis-diMe 3-methyl-4-cyclohexene-1,2-dicarboxylate (III), b20 144-5.degree., 1.1101, 1.4706; trans-di-Et 3-methyl-4-cyclohexene-1,2-dicarboxylate (IV), b20 152-3.degree., 1.0409, 1.4604; cis-di-Me 4-methyl-4-cyclohexene-1,2-dicarboxylate (V), b20 149-50.degree., 1.1139, 1.4735; trans-di-Et 4-cyclohexene-1,2-dicarboxylate (VI), b20 160-1.degree., 1.0480, 1.4620; cis-di-Me 3,6-dimethyl-4-cyclohexene-1,2-dicarboxylate (VII), b20 154.5-5.5.degree., 1.0989, 1.4736; trans-di-Et 3,6-dimethyl-4-cyclohexene-1,2-dicarboxylate, b10 148.5-9.5.degree., 1.0389, 1.4650 (VIII). MeMgI from 6 g. Mg with 31.5 g. I gave 3.5 g. diketone and 5.3 g. cis-1-acetyl-2-isopropenyl-4-cyclohexene, b20 93-5.degree., d20 0.9660, nD20 1.4908; the diketone, 1,2-diacetyl-4-cyclohexene, m. 70.degree., treated with MeMgI gave 51% 1,2-bis(1-hydroxyisopropyl)-4-cyclohexene, m. 119.5-20.degree.. MeMgI from 18 g. Mg with 29.7 g. I gave 76.9% of the latter glycol; this distd. from (CO2H)2 (10% soln.) gave 28% hexahydrobenzofuran, b20 97.5-8.5.degree., d20 0.9441, nD20 1.4778. MeMgI from 6 g. Mg and 23.5 g. II gave 5.4 g. corresponding 1,2-diacetyl-4-cyclohexene, m. 114.degree., and 7 g. trans-1-acetyl-2-isopropenyl-4-cyclohexene, b20 91-2.degree., d20 0.9630, nD20 1.4872 (the infrared spectrum shows the C:C and C:O bands at 1645 and 1720 cm.-1); the latter was unaffected by heating with AcOH-HCl. The diketone (5.4 g.) and MeMgI from 4 g. Mg gave 55.8% 1,2-bis(1-hydroxyisopropyl)-4-cyclohexene, isomer, m. 105-6.degree., also formed in 66.6% yield from 31.5 g. II and MeMgI from 19 g. Mg. MeMgI from 7.2 g. Mg and 21.2 g. III gave 4.8 g. cis-1-acetyl-2-isopropenyl-6-methyl-4-cyclohexene, b20 100-2.degree., d20 0.9349, nD20 1.4838, and 8.6 g. mixed 1,2-diacetyl-3-methyl-4-cyclohexene and 1,2-bis(1-hydroxyisopropyl)-3-methyl-4-cyclohexene; the mixt. (12 g.) heated 6 hrs. to 200.degree. with 12 g. Ac2O, then steam distd. gave 2.3 g. pure diketone, m. 101-2.degree., and 4.1 g. methylhexahydrobenzofuran, b20 103.5-4.5.degree., d20 0.9302, nD20 1.4745. III (32 g.) with MeMgI from 18 g. Mg gave 2.7 g. above diketone and 16 g. mixed oxo alc. and glycol, above. MeMgI from 15 g. Mg and 26.2 g. IV gave 13.4 g. mixed diketone and glycol, which heated as above with 25 g. Ac2O 12 hrs. at 230-40.degree. gave 4.5 g. 1,2-diacetyl-3-methyl-4-cyclohexene, m. 97.5-8.5.degree., and 4.4 g. hydrocarbons. MeMgI from 18 g. Mg and 32.2 g. V gave 61.8%

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1,2-bis(1-hydroxyisopropyl)-4-methyl-4-cyclohexene, m. 81.5-2.5.degree., which heated with Ac2O 6 hrs. at 200.degree. gave the corresponding methylhexahydrobenzofuran, b20 103-5.degree., d20 0.9268, nD20 1.4778. MeMgI from 2 g. Mg with 7 g. V gave 42% cis-1-acetyl-2-isopropenyl-4-methyl-4-cyclohexene, b20 110-12.degree., d20 0.9355, nD20 1.4830. MeMgI from 14 g. Mg and 25 g. VI gave 95.4% 1,2-bis(1-hydroxyisopropyl)-4-cyclohexene, m. 95-6.degree., while with lower proportion of MeMgI there was obtained 52.5% trans-1-acetyl-2-isopropenyl-4-methyl-4-cyclohexene, b20 106-8.degree., d20 0.9432, nD20 1.4851. MeMgI from 12 g. Mg and 22.6 g. VII gave 37.5% cis-1-acetyl-2-isopropenyl-3,6-dimethyl-4-cyclohexene, b20 109-10.degree., d20 0.9297, nD20 1.4830. Similarly MeMgI from 12 g. Mg and 23.4 g. VIII gave 37.8% trans-1-acetyl-2-isopropenyl-3,6-dimethyl-4-cyclohexene, b20 103.5-4.degree., d20 0.9376, nD20 1.4905. The glycols described above were dehydrated by heating with excess Ac2O in sealed tubes 12 hrs. at 230-40.degree., yielding after steam distn. mixts. of satd. and unsatd. hydrocarbons. Thus, cis-1,2-bis(1-hydroxyisopropyl)-4-cyclohexene gave a hydrocarbon mixt., b20 91-2.5.degree., d20 0.8733, nD20 1.4960; the trans isomer gave a mixt. b20 91-2.degree., 0.8824, 1.5028. cis-1,2-Bis(1-hydroxyisopropyl)-3-methyl-4-cyclohexene gave hydrocarbons, b20 105-7.degree., 0.9023, 1.5084, while the trans isomer gave hydrocarbons, b20 104.5-6.degree., 0.8821, 1.5021. cis-1,2-Bis(1-hydroxyisopropyl)-4-methyl-4-cyclohexene gave hydrocarbons, b20 106-6.5.degree., 0.8781, 1.4968, while the trans isomer gave hydrocarbons, b20 105.5-6.degree., 0.8743, 1.4985. Treatment of some of these with Br indicated the presence of varying amt. of olefinic materials in addn. to aromatic products.

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ACCESSION NUMBER: 1957:9169 CAPLUS
DOCUMENT NUMBER: 51:9169
ORIGINAL REFERENCE NO.: 51:1866g-i,1867a-i,1868a-i
TITLE: Nitroalkanes from conjugated nitroalkenes by reduction with complex hydrides
AUTHOR(S): Schechter, H.; Ley, D. E.; Roberson, E. B., Jr.
CORPORATE SOURCE: Ohio State Univ., Columbus
SOURCE: J. Am. Chem. Soc. (1956), 78, 4984-91
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
AB PrCH(NO2)CH(OH)Et (I) (248.3 g.), light yellow liquid, b0.5 71.0-1.5.degree., nD20 1.4475, d2020 1.0324, MRD 41.76, was prepd. in 77% yield by heating 116.2 g. PrOH, 206.2 g. BuNO2, and 23 cc. 3.5N NaOH in 200 cc. 95% EtOH 48 hrs. at 30-5.degree.. I (193.4 g.) treated 2.5 hrs. at 40-50.degree. with 128.6 g. Ac2O and 1 cc. H2SO4 gave 216.9 g. acetate (II) of I, colorless liquid, b0.1 69.degree., nD20 1.4352, d2020 1.0409, MRD 50.97. II (131.5 g.) and 6.6 g. NaOAc heated at 115.degree., and the distillate, b12 75-80.degree., dissolved in Et2O, washed with satd. aq. NaHCO3, dried, and distd. yielded 67.6 g. PrC(NO2):CHEt (III), light green lacrimatory liquid, b5.2 70.0-70.8.degree., nD20 1.4585. MeNO2 (92.0 g.), 76.0 g. CF3CH(OH)2-H2O azeotrope, and 4.0 g. Na2CO3 kept 4 hrs. at 50.degree. and 15 hrs. at 25-30.degree. gave 64.4 g. CF3CH(OH)CH2NO2 (IV), colorless liquid, b5.5 62-6.degree., nD20 1.3792. IV (45.5 g.) and 45.5 g. phthalic anhydride heated to 140-80.degree., and the distillate dissolved in Et2O, dried, and fractionated yielded 19.2 g. CF3CH: CHNO2 (V), yellow-green lacrimator, b. 89.degree., nD20 1.3609, d2020 1.423. IV (50.1 g.) added with stirring to 50.0 g. P2O5 at such a rate that the product distd. off, the residue heated in vacuo, and the combined distillates rectified yielded 30.2 g. V, b. 89-90.degree., nD20 1.3607, d2020 1.423. CF3Ac (30.1 g.) added dropwise with stirring at 0.degree. to 565 g. MeNO2 and 4.0 g. K2CO3, and the mixt. stirred 3 days at 20-30.degree., neutralized, dried, and distd. gave 29.3 g. Me(CF3)C(OH)CH2NO2 (VI), b3 42-3.degree., nD20 1.3881, d2020 1.2302. AcCl (41.6 g.) and 81.0 g. VI kept 20 hrs. at 30.degree. and distd. yielded 88.4 g. acetate (VII) of VI, b30 93.5-4.5.degree., nD20 1.3905. VI (60.0 g.) added dropwise with stirring to 60.0 g. P2O6 at 190-200.degree. during 3 hrs., and the light green distillate fractionated gave 11.2 g. VI and 34.4 g. Me(CF3)C:CHNO2 (VIII), green powerful lacrimator, b200 79-82.degree., nD20 1.3791, d2020 1.353. VII (40.0 g.) in 100 cc. Et2O stirred with 10% aq. NaHCO3 until the CO2 evolution ceased, dried, and distd. gave 6.05 g. VIII, b210 80.0-80.5.degree., nD20 1.3785. CH2:C(NO2)Et (IX) (15.2 g.) in 25 cc. Et2O added in 70 min. with stirring to 28.8 g. NaBH(OMe)3 (X) in 125 cc. Et2O and 50 cc. tetrahydrofuran at -60 to -65.degree., the mixt. stirred 0.5 hr. at -60 to -65.degree., acidified in 1 hr. at 0.degree. with aq. AcOH-urea and satd. with NaCl, the aq. layer (XI) extd. with Et2O, and the combined org. layer and ext. worked up gave 6.95 g. EtMeCHNO2 (XII), colorless liquid, b80 60-70.degree., b742.3 137.5.degree., nD20 1.4048-1.4050 (redistd. b756.4

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138.5.degree., nD20 1.4044); 5.34 g. MeEtC(NO2)CH2CH(NO2)Et (XIII), b0.5 86-90.degree., nD20 1.4568-1.4577 (redistd., b0.7 79-81.degree., nD20 1.4573, d2020 1.1125, MRD 50.03). XIII was converted via the Nef reaction [cf. Ann. 280, 263 (1894)] to EtMeC(NO2)CH2COEt [2,4-dinitrophenylhydrazone (XIV), m. 131.5-2.5.degree.. IX (0.15 mole) in 25 cc. Et2O added dropwise with stirring at -1 .+-. 1.degree. during 1.5 hrs. to 0.165 mole X in 125 cc. Et2O and 50 cc. tetrahydrofuran, and the mixt. worked up after 1.5 hrs. in the usual manner gave 18% recovered IX, 9% XII, 5% XIII, and 68% unidentified polymers. IX (0.12 mole) in Et2O added similarly at -58 .+-. 2.degree. to 0.132 mole X during 1.2 hrs. and worked up after 0.5 hr. yielded 17% recovered IX, 30% XII, 46% XIII, and 7% polymer. IX (0.15 mole) in 25 cc. Et2O added dropwise with stirring during 1.5 hrs. at -1 .+-. 1.degree. to 0.0375 mole LiBH4 in 125 cc. Et2O and 50 cc. tetrahydrofuran, the mixt. worked up in the usual manner after 1.5 hrs., and the crude product extd. with NaHSO3 to remove unreacted IX and then distd. gave 45% unchanged IX, 16% XII, 23% XIII, and 16% polymers. A similar run at -52 .+-. 1.degree. with 0.8 hr. addn. time and 1.1 hrs. reaction time gave 67% unreacted IX, 24% XII, 6% XIII, and 3% polymers. Another run carried out at -69 .+-. 1.degree. with 3 hrs. addn. time and 5.5 hrs. reaction time gave 40% unreacted IX, 39% XII, 9% XIII, and 12% polymer; this run repeated but with 0.52 mole LiBH4 gave 8% unreacted IX, 59% XII, 14% XIII, and 19% polymers. IX (4.45 g.) added in 35 min. to 4.54 g. XII and 2.91 g. KOH in 20 cc. EtOH, the mixt. acidified below 0.degree. and extd. with Et2O, and the ext. worked up gave 2.64 g. XIII, b1 80-5.degree., nD20 1.4565, d2020 1.1132, which was converted in 52% yield by the Nef reaction to XIV. C3F7CH:C(NO2)Et (XV) (15.34 g.) in 25 cc. Et2O added during 4 hrs. to 0.62 g. LiBH4 in 125 cc. Et2O and 50 cc. tetrahydrofuran at -60 .+-. 2.degree. with stirring, and the mixt. stirred 4 hrs. at -60.degree., acidified below 0.degree. in 45 min., and worked up gave 14.08 g. C3F7CH2CH(NO2)Et (XVI), b24.5-25.0 79.0-9.5.degree., nD20 1.3493, b23-25 78.5-9.0.degree., nD20 1.3488, d2020 1.4286. XV treated similarly at -60.degree. with 2.0 hrs. addn. time and 1.0 hr. reaction time with X at -60 gave 91% conversion to XVI. XV treated with LiAlH4 at -70.degree. with 3 hrs. addn. time and 3.5 hrs. reaction time at -70.degree. gave 85% conversion to XVI. XVI (1.00 g.) in 10 cc. MeOH added to 0.4 g. NaOH and 10 cc. H2O, the mixt. kept 18 hrs. at 0.degree. and added dropwise at 0.degree. to 2.5 cc. concd. H2SO4 and 12 cc. H2O and treated with 2,4-(O2N)2C6H3NHNH2 in H2SO4 gave 0.83 g. 2,4-(O2N)2C6H3NHN:CEtCH2C3F7, orange needles, m. 123-4.degree.. MeCH:CHNO2 (0.15 mole) added in the usual manner in 25 cc. Et2O at -70.degree. during 1.2 hrs. to 0.225 mole X in 125-150 cc. Et2O and 50 cc. tetrahydrofuran and worked up in the usual manner gave 82% conversion to EtCH2NO2 (XVII), b742 129.degree., nD20 1.4023, and 11% conversion to EtCH(NO2)CHMeCHO2NO2 (XVIII), b0.8 86.3.degree., nD20 1.4558, d2020 1.1707. MeCH:CHNO2 (0.15 mole) in 25 cc. Et2O added to 0.075 mole LiBH4 in 125 cc. Et2O and 25 cc. tetrahydrofuran at -70.degree. during 3 hrs., and the mixt. worked up after 2 hrs. gave 50% conversion to XVII and 2% to XVIII. IX reduced in the usual manner at -70.degree. during 2.5 hrs. with

L33 ANSWER 18 OF 18 CAPLUS COPYRIGHT 2001 ACS (Continued)
3 hrs. addn. time and worked up gave 59% conversion to XII and 14% conversion to XIII. IX (0.10-0.15 mole) in 25-50 cc. Et2O added to 0.05 mole NaBH4 in 100-150 cc. Et2O and 0-25 cc. tetrahydrofuran during 3 hrs. and worked up after 4 hrs. gave 64% conversion to XII and 4% conversion to XIII. MeCH:C(NO2)Me (XIX) reduced in the usual manner with X at -70.degree. with 1.1 hr. addn. time and 0.6 hr. reaction time gave 63% conversion to XII and 11% to EtMeC(NO2)CHMeCH(NO2)Me (XX), b0.1 78-80.degree., nD20 1.4657, d2020 1.126. XIX reduced with LiBH4 (2.5 hrs. each addn. and reaction time) at -37.degree. gave 46% conversion to XII. XIX reduced with LiAlH4 at -65.degree. (2.5 hrs. addn. and 3.5 hrs. reaction time) gave 53% conversion to XII. Me2C:CHNO2 (XXI) reduced with X at -3.degree. (1.4 hrs. addn. and 0.6 hr. reaction time) yielded 59% conversion to Me2CCHCH2NO2 (XXII), b70 69-70.7.degree., nD20 1.4090, d2020 0.9627; similar reduction of XXI with LiBH4 at 0.degree. (0.5 hr. addn. and 3 hrs. reaction time) gave 48% conversion to XXII. III reduced with X at 0.degree. (3.0 hrs. each addn. and reaction time) gave 55% conversion to Pr2CHNO2 (XXIII), b9 70-1.degree., nD20 1.4224-1.4236, d2020 0.9269. III reduced with LiBH4 at -67.degree. (4 hrs. each addn. and reaction time) gave 65% conversion to XXIII. III reduced with LiAlH4 (2 hrs. addn. and 7 hrs. reaction time) gave 22% conversion to XXIII. CCl3CH:CHNO2 (XXIV) reduced at -40.degree. with X (1.1 hrs. addn. and 0.5 hr. reaction time) gave 44% conversion to CCl3(CH2)2NO2 (XXV), b3 70.0-1.3.degree., nD20 1.4899, d2020 1.5347, and 26% conversion to CCl3CH2CH(NO2)CH(CCl3)CH2NO2 (XXVI), m. 150-1.degree.. XXIV reduced at -70.degree. with LiBH4 (3.5 hrs. addn. and reaction time) gave 85% conversion to XXV; a similar run with LiAlH4 gave 44% conversion to XXV. V treated at -40.degree. with LiAlH4 (2 hrs. addn. and 3 hrs. reaction time) gave 25% conversion to CF3(CH2)2NO2, b750.6 132.degree., nD20 1.3549-1.3555, d2020 1.4203, and 25% conversion to CF3CH2CH(NO2)CH(CF3)CH2NO2, b0.9 76.9.degree., nD20 1.3910, d2020 1.6181. VIII reduced with LiAlH4 at -70.degree. (1.5 hrs. addn. and 3 hrs. reaction time) gave 55% conversion to Me(CF3)CHCH2NO2, b150 83.5-84.degree., d2020 1.312. C3F7CH:C(NO2)Me (XXVII) reduced at -67.degree. with X (2.0 hrs. addn. and 1.0 hr. reaction time) gave 84% conversion to C3F7CH2CH(NO2)Me (XVIII), b39-40 77-8.8.degree., nD20 1.3407, d2020 1.4861. XXVII reduced at -65.degree. with LiBH4 (4 hrs. each addn. and reaction time) gave 88% conversion to XXVIII. PhCH:CHNO2 (XXIX) reduced at -40.degree. (1.6 hrs. addn. and 0.4 hr. reaction time) gave 39% conversion to Ph(CH2)2NO2 (XXX), b0.5 73-4.5.degree., nD20 1.5270, d2020 1.1314, and 24% conversion to PhCH2CH(NO2)CHPhCH2NO2 (XXXI), m. 120.5-1.0.degree.. XXIX reduced at -70.degree. with LiBH4 (3 hrs. addn. and 0.25 hr. reaction time) gave 55% conversion to XXX. XXIX reduced with NaBH4 (5 hrs. addn. and 1 hr. reaction time) gave 14 and 24% conversion to XXX and XXXI, resp. XXIX reduced at -40.degree. with LiAlH4 (2.2 hrs. addn. and 3 hrs. reaction time) gave 50 and 6% conversion to XXX and XXXI, resp.; inverse addn. gave 47 and 7% conversion, resp. PhCH:C(NO2)Me reduced at -40.degree. with LiAlH4 (2 hrs. addn. and 3 hrs. reaction time) gave 43% conversion to PhCH2CH(NO2)Me, b0.8 81.5-82.degree., nD25 1.5214; inverse addn. gave 31% conversion. 2-(2-Nitrovinyl)furan (XXXII) reduced at -40.degree. with X (1.8 hrs. addn. and 0.9 hr. reaction time) gave 28% conversion to 2-(2-nitroethyl)furan (XXXIII), b2.0 61.5-3.0.degree., nD20 1.4843, d2020

L33 ANSWER 18 OF 18 CAPLUS COPYRIGHT 2001 ACS (Continued)
1.2052. XXXII reduced with LiBH4 at -73.degree. (5 hrs. addn. and 0.25 hr. reaction time) gave 31% conversion to XXXIII. XXXII reduced with LiAlH4 at -55.degree. (3 hrs. addn. and 3.5 hrs. reaction time) gave 16% conversion to XXXIII. D-arabo-Tetraacetoxy-1-nitro-1-hexene (XXXIV) (1.81 g.) in 10 cc. Et2O and 4 cc. tetrahydrofuran added during 70 min. with stirring to 0.11 g. LiBH4 in 15 cc. Et2O and 5 cc. tetrahydrofuran at 0.degree., the mixt. stirred 2 hrs. at 0.degree., acidified during 15 min. below 0.degree. with aq. AcOH-urea, and satd. with NaCl, and the Et2O layer worked up yielded 1.37 g. crude 1-nitro-1,2-dideoxy-D-arabo-hexitol tetraacetate (XXXV), m. 63-73.degree.. Crude XXXV heated with 15 cc. Ac2O and 1 drop concd. H2SO4 1 hr. at 85-95.degree. and evapd. in vacuo, and the residue dild. with Et2O and cooled gave 0.99 g. pure XXXV, white solid, m. 90-2.degree. (from Et2O). XXIV (1.00 g.) in 10 cc. abs. EtOH added in 45 min. at 0.degree. with stirring to 0.12 g. NaBH4, the mixt. stirred 2 hrs. at 0.degree., acidified in 10 min. below 0.degree., concd. in vacuo to about 5 cc. and dild. with Et2O, and the soln. dried and worked up gave 0.65 g. XXXV, m. 91-2.degree. (from Et2O).

L19 ANSWER 9 OF 10 CAPLUS COPYRIGHT 2001 ACS
ACCESSION NUMBER: 1988:492343 CAPLUS
DOCUMENT NUMBER: 109:92343
TITLE: Preparation of isopropylmethylbutenoylcyclohexanes, -cyclohexenes, -cyclohexadienes, and perfume compositions thereof
INVENTOR(S): Van der Weerdt, Antonius Johannes; Broekhof, Nicolaas Leonardus Johanna; Witteveen, Jan Gerardus
PATENT ASSIGNEE(S): Naarden International N. V., Neth.
SOURCE: Eur. Pat. Appl., 13 pp.
CODEN: EPXXDW
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
EP 231556	A1	19870812	EP 1986-202370	19861223
R: CH, DE, ES, FR, GB, LI, NL				
US 4760050	A	19880726	US 1987-2391	19870109
JP 62169743	A2	19870725	JP 1987-11478	19870122

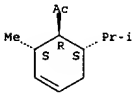
PRIORITY APPLN. INFO.: NL 1986-152 19860123

AB The title compds. (I) were prepd. as fragrances with fruity flowery and green odors, in some cases accompanied by wood and/or herbal notes. Thus, trans-5-methyl-3-hexene-2-one in cyclohexane was added to AlCl3 in cyclohexane under ice cooling. Piperylene in cyclohexane was added to the resulting mixt. at 60.degree. over 2 h and the mixt. was stirred for an addnl. 2 h to give cis- and trans-2-acetyl-1-isopropyl-3-methyl-4-cyclohexane. The latter in C6H6 were added to a refluxed mixt. of EtMgBr and PhNHMe in C6H6. MeCHO in C6H6 was then added at -15.degree. to give, after dehydration, cis- and trans-1-isopropyl-3-methyl-2-(but-2-enoyl)-4-cyclohexene.

IT **115865-78-6P 115865-82-2P 115938-79-9P**
RL: **RCT (Reactant)**; SPN (Synthetic preparation); **PREP (Preparation)**
(prepn. and aldol reaction of, with acetaldehyde)

RN 115865-78-6 CAPLUS
CN Ethanone, 1-[2-methyl-6-(1-methylethyl)-3-cyclohexen-1-yl]-, (1.alpha.,2.beta.,6.beta.)- (9CI) (CA INDEX NAME)

Relative stereochemistry.



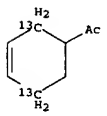
RN 115865-82-2 CAPLUS
CN Ethanone, 1-[6-methyl-2-(1-methylethyl)-1,3-cyclohexadien-1-yl]- (9CI) (CA INDEX NAME)

L19 ANSWER 10 OF 10 CAPLUS COPYRIGHT 2001 ACS
ACCESSION NUMBER: 1986:129206 CAPLUS
DOCUMENT NUMBER: 104:129206
TITLE: A new method for studying chain conformation. Proof of nonradial binding to micelles: chain-bending at an enzyme surface
AUTHOR(S): Menger, F. M.; Carnahan, D. W.
CORPORATE SOURCE: Dep. Chem., Emory Univ., Atlanta, GA, 30322, USA
SOURCE: J. Am. Chem. Soc. (1986), 108(6), 1297-8
CODEN: JACSAT; ISSN: 0002-7863
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 104:129206

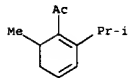
AB A method is developed which uses 3JCC of di-13C-labeled compds. to det. chain conformation. The method is used to prove that bolaform electrolytes bind nonradially to micelles and that a dicationic bolaform bends when binding to an enzyme surface.

IT **100313-03-9P**
RL: **RCT (Reactant)**; SPN (Synthetic preparation); **PREP (Preparation)**
(prepn. and hydrogenation of)

RN 100313-03-9 CAPLUS
CN Ethanone, 1-(3-cyclohexen-1-yl-2,5-13C2)- (9CI) (CA INDEX NAME)

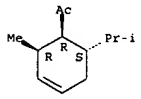


L19 ANSWER 9 OF 10 CAPLUS COPYRIGHT 2001 ACS (Continued)



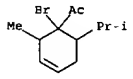
RN 115938-79-9 CAPLUS
CN Ethanone, 1-[2-methyl-6-(1-methylethyl)-3-cyclohexen-1-yl]-, (1.alpha.,2.alpha.,6.beta.)- (9CI) (CA INDEX NAME)

Relative stereochemistry.



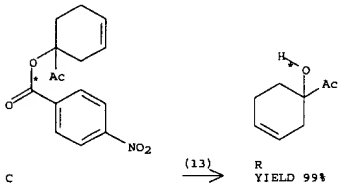
IT **115865-81-1P**
RL: **RCT (Reactant)**; SPN (Synthetic preparation); **PREP (Preparation)**
(prepn. and dehydrohalogenation of)

RN 115865-81-1 CAPLUS
CN Ethanone, 1-[1-bromo-2-methyl-6-(1-methylethyl)-3-cyclohexen-1-yl]- (9CI) (CA INDEX NAME)



L10 ANSWER 1 OF 4 CASREACT COPYRIGHT 2001 ACS
ACCESSION NUMBER: 132:151501 CASREACT
TITLE: Captodative olefin 3-(4-nitrobenzoyloxy)-3-buten-2-one as a Diels-Alder ketene equivalent for the synthesis of .gamma.-hydroxycyclohexenones
AUTHOR(S): Ochoa, Maria E.; Arias, Maria S.; Aguilar, Raul; Delgado, Francisco; Tamariz, Joaquin
CORPORATE SOURCE: Departamento de Quimica Organica, Escuela Nacional de Ciencias Biologicas, I.P.N., Mexico, D.F., 11340, Mex.
SOURCE: Tetrahedron (1999), 55(51), 14535-14546
CODEN: TETRAB; ISSN: 0040-4020
PUBLISHER: Elsevier Science Ltd.
DOCUMENT TYPE: Journal
LANGUAGE: English
AB A short and regioselective synthesis of .gamma.-hydroxycyclohexenones is described, using 3-(4-nitrobenzoyloxy)-3-buten-2-one as a ketene equiv. in Diels-Alder reactions with substituted dienes. Oxidn. with MCPBA of the .alpha.-acetylcyclohexenol deriv., obtained by hydrolysis of the cycloadducts, led to the corresponding .gamma.-hydroxycyclohexenones in moderate overall yields. Evidence of the mechanism is provided.

RX(13) OF 32 ...C ===> R...



C → R
YIELD 99%

RX(13) RCT C **258266-14-7**

STAGE(1)
RGT AG 584-08-7 K2CO3
SOL 75-09-2 CH2Cl2, 67-56-1 MeOH

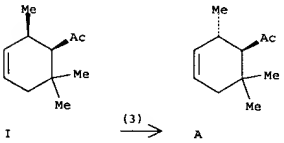
STAGE(2)
SOL 75-09-2 CH2Cl2
PRO R **82873-57-2**
NTE STEREOSELECTIVE

REFERENCE COUNT: 68
REFERENCE(S): (1) Aggarwal, V; Tetrahedron 1999, V55, P293 CAPLUS
(2) Aguilar, R; Tetrahedron Lett 1987, V28, P865

L10 ANSWER 1 OF 4 CASREACT COPYRIGHT 2001 ACS (Continued)
CAPLUS
(3) Alcaraz, L; Tetrahedron Lett 1996, V37, P6619 CAPLUS
(4) Andrade, R; Synth Commun 1992, V22, P1603 CAPLUS
(5) Arai, Y; Synth Commun 1986, V16, P233 CAPLUS
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L10 ANSWER 2 OF 4 CASREACT COPYRIGHT 2001 ACS
ACCESSION NUMBER: 119:203029 CASREACT
TITLE: Preparation and scent of .delta.-damascone and its analogs
AUTHOR(S): Andreev, V. M.; Andreeva, L. K.; Ratnikova, E. V.; Fomchenko, Z. V.; Grigor'eva, L. T.
CORPORATE SOURCE: VNII Sint. Nat. Dushistykh Veshchestr, Russia
SOURCE: Gidroliz. Lesokhim. Prom-st. (1993), (1), 23-4
CODEN: GLKPA2; ISSN: 0016-9706
DOCUMENT TYPE: Journal
LANGUAGE: Russian
AB Diels-Alder reaction of CH2:CRCH:CHR1 (R = H, R1 = H, Me; R = Me, R1 = H) with 5 equiv MeCOCR2:CMeR3 (R2 = H, R3 = Me; R2 = Me, R3 = H) in PhMe contg. 5 mol% AlCl3 at 35-40.degree. gave .ltoreq.81% yields of 5 corresponding acetylcyclohexene adducts I (R4 = Me). These underwent aldol condensation with MeCHO and subsequent dehydration to give .ltoreq.48% title compds. I (same R-R3, R4 = CH:CHMe). These products had fruity, woody, or camphor-like odors with spicy or vegetable notes.

RX(3) OF 7 ...I ===> A...

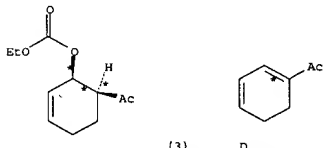


I → A
YIELD 100%

RX(3) RCT I **41436-48-0**
RGT L 1310-58-3 KOH
PRO A **41435-93-2**
SOL 64-17-5 EtOH

L10 ANSWER 3 OF 4 CASREACT COPYRIGHT 2001 ACS
ACCESSION NUMBER: 113:152772 CASREACT
TITLE: O-1-(1,3-Butadienyl) carbamates as Diels-Alder dienes: stereospecific synthesis of (.+-.)-hernandulcin and congeners
AUTHOR(S): De Cusati, Paul F.; Olofson, R. A.
CORPORATE SOURCE: Dep. Chem., Pennsylvania State Univ., University Park, PA, 16802, USA
SOURCE: Tetrahedron Lett. (1990), 31(10), 1409-12
CODEN: TELEAY; ISSN: 0040-4039
DOCUMENT TYPE: Journal
LANGUAGE: English
AB The TiCl4-catalyzed addn. of the title reactants, e.g., RCO2CH:CHCH:CH2 (R = OEt, NEt2) to vinyl ketones, e.g., MeCOCH:CH2, regio- and stereospecifically yields cis-disubs. cyclohexenes I which add RMgX stereospecifically to the ketone. A final product in this sequence is the intensely sweet sesquiterpene, hernandulcin (II).

RX(3) OF 39 ...C ===> D



C → D
YIELD 87%

RX(3) RCT C **129447-03-6**
RGT H 12125-02-9 NH4Cl
PRO D **53329-13-8**
SOL 7732-18-5 Water, 123-91-1 Dioxane

L10 ANSWER 4 OF 4 CASREACT COPYRIGHT 2001 ACS

ACCESSION NUMBER: 112:97817 CASREACT

TITLE: Highly selective Diels-Alder cycloadditions of captodative dienophiles 1-acetylvinyl arenecarboxylates to unsymmetrically substituted butadienes

AUTHOR(S): Reyes, Alicia; Aguilar, Raul; Munoz, Alfredo H.; Zwick, Jean Christophe; Rubio, Manuel; Escobar, Jose Luis; Soriano, Manuel; Toscano, Ruben; Tamariz, Joaquin

CORPORATE SOURCE: Esc. Nac. Cienc. Biol., IPN, Mexico City, 11340, Mex.

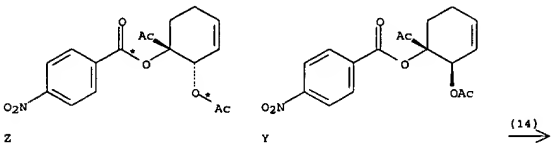
SOURCE: J. Org. Chem. (1990), 55(3), 1024-34
CODEN: JOCEAH; ISSN: 0022-3263

DOCUMENT TYPE: Journal

LANGUAGE: English

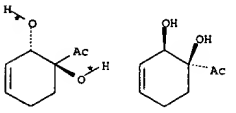
AB Thermal Diels-Alder cycloaddns. of captodative olefins 1-acetylvinyl arenecarboxylates, CH2:C(COCH3)OCOAr (Ar = p-C6H4NO2, .alpha.-naphthyl and .beta.-naphthyl), with isoprene were regioselective. This regioselectivity was greatly improved by using Lewis acids catalysts (ZnCl2, BF3.cntdot.Et2O), the para adduct being the main isomer. Stereoselectivity of these reactions was examd. Regioselectivity of these cycloaddns. has been rationalized by MINDO/3 and ab initio methods.

RX(14) OF 23 ...Z + Y ===> AG + AH...



Z Y

(14)



AG
YIELD 95%(95)

AH
YIELD 95%(5)

RX(14) RCT Z 111945-70-1, Y 111945-71-2

L10 ANSWER 4 OF 4 CASREACT COPYRIGHT 2001 ACS (Continued)

RGT R 584-08-7 K2CO3

PRO AG 125229-00-7, AH 125229-01-8

SOL 75-09-2 CH2Cl2

09/875,158

=> d ibib ab hitstr 1-10

L19 ANSWER 1 OF 10 CAPLUS COPYRIGHT 2001 ACS
ACCESSION NUMBER: 1999:798078 CAPLUS
DOCUMENT NUMBER: 132:151501
TITLE: Captodative olefin 3-(4-nitrobenzoyloxy)-3-buten-2-one as a Diels-Alder ketene equivalent for the synthesis of .gamma.-hydroxycyclohexenones
AUTHOR(S): Ochoa, Maria E.; Arias, Maria S.; Aguilar, Raul; Delgado, Francisco; Tamariz, Joaquin
CORPORATE SOURCE: Departamento de Quimica Organica, Escuela Nacional de Ciencias Biologicas, I.P.N., Mexico, D.F., 11340, Mex.
SOURCE: Tetrahedron (1999), 55(51), 14535-14546
CODEN: TETRAB; ISSN: 0040-4020
PUBLISHER: Elsevier Science Ltd.
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 132:151501

AB A short and regioselective synthesis of .gamma.-hydroxycyclohexenones is described, using 3-(4-nitrobenzoyloxy)-3-buten-2-one as a ketene equiv. in Diels-Alder reactions with substituted dienes. Oxidn. with MCPBA of the .alpha.-acetylcyclohexenol deriv., obtained by hydrolysis of the cycloadducts, led to the corresponding .gamma.-hydroxycyclohexenones in moderate overall yields. Evidence of the mechanism is provided.

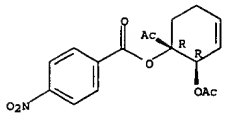
IT **82873-57-2P 111945-71-2P 258266-09-0P 258266-12-5P 258266-13-6P 258266-14-7P 258266-16-9P**
RL: **RCT (Reactant)**; SPN (Synthetic preparation); **PREP (Preparation)**
(prepn. of .gamma.-hydroxycyclohexenones via Diels-Alder reaction of [(nitrobenzoyl)oxy]butenone (ketene equiv.))

RN 82873-57-2 CAPLUS
CN Ethanone, 1-(1-hydroxy-3-cyclohexen-1-yl)- (9CI) (CA INDEX NAME)

RN 111945-71-2 CAPLUS
CN Ethanone, 1-[(1R,2R)-2-(acetyloxy)-1-[(4-nitrobenzoyl)oxy]-3-cyclohexen-1-yl]-, rel- (9CI) (CA INDEX NAME)

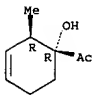
Relative stereochemistry.

L19 ANSWER 1 OF 10 CAPLUS COPYRIGHT 2001 ACS (Continued)



RN 258266-09-0 CAPLUS
CN Ethanone, 1-[(1R,2R)-1-hydroxy-2-methyl-3-cyclohexen-1-yl]-, rel- (9CI) (CA INDEX NAME)

Relative stereochemistry.

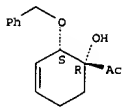


RN 258266-12-5 CAPLUS
CN Ethanone, 1-[(1R,2R)-2-(acetyloxy)-1-hydroxy-3-cyclohexen-1-yl]-, rel- (9CI) (CA INDEX NAME)

Relative stereochemistry.

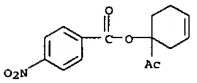
RN 258266-13-6 CAPLUS
CN Ethanone, 1-[(1R,2S)-1-hydroxy-2-(phenylmethoxy)-3-cyclohexen-1-yl]-, rel-
(9CI) (CA INDEX NAME)

Relative stereochemistry.



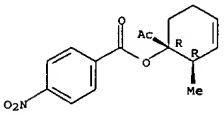
L19 ANSWER 1 OF 10 CAPLUS COPYRIGHT 2001 ACS (Continued)

RN 258266-14-7 CAPLUS
CN Ethanone, 1-[1-[(4-nitrobenzoyl)oxy]-3-cyclohexen-1-yl]- (9CI) (CA INDEX NAME)



RN 258266-16-9 CAPLUS
CN Ethanone, 1-[(1R,2R)-2-methyl-1-[(4-nitrobenzoyl)oxy]-3-cyclohexen-1-yl]-, rel- (9CI) (CA INDEX NAME)

Relative stereochemistry.



IT **125229-00-7P**
RL: SPN (Synthetic preparation); **PREP (Preparation)**
(prepn. of .gamma.-hydroxycyclohexenones via Diels-Alder reaction of [(nitrobenzoyl)oxy]butenone (ketene equiv.))

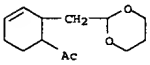
RN 125229-00-7 CAPLUS
CN Ethanone, 1-[(1R,2R)-1,2-dihydroxy-3-cyclohexen-1-yl]-, rel- (9CI) (CA INDEX NAME)

Relative stereochemistry.

REFERENCE COUNT: 68
REFERENCE(S):
(1) Aggarwal, V; Tetrahedron 1999, V55, P293 CAPLUS
(2) Aguilar, R; Tetrahedron Lett 1987, V28, P865 CAPLUS
(3) Alcaraz, L; Tetrahedron Lett 1996, V37, P6619 CAPLUS
(4) Andrade, R; Synth Commun 1992, V22, P1603 CAPLUS
(5) Arai, Y; Synth Commun 1986, V16, P233 CAPLUS
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L19 ANSWER 1 OF 10 CAPLUS COPYRIGHT 2001 ACS (Continued)

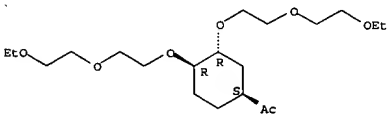
L19 ANSWER 2 OF 10 CAPLUS COPYRIGHT 2001 ACS
ACCESSION NUMBER: 1999:399412 CAPLUS
DOCUMENT NUMBER: 131:228583
TITLE: Synthesis of 11-deoxydaunomycinone and novel 10-fluoroanthracyclinone derivatives
AUTHOR(S): Rho, Young S.; Choi, Younghee; Kim, Gyuil; Sin, Hongsig; Yoo, Dong Jin; Kim, Sun-Ha; Cheong, Chaejoon
CORPORATE SOURCE: Department of Chemistry, Chonbuk National University, Jeonju, 561-756, S. Korea
SOURCE: Bull. Korean Chem. Soc. (1999), 20(5), 551-555
CODEN: BKCSDE; ISSN: 0253-2964
PUBLISHER: Korean Chemical Society
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 131:228583
AB 11-Deoxydaunomycinone I and 10-fluoroanthracyclinone derivs. II (.beta.-F,.alpha.-OH; .alpha.-F,.beta.-OH) were obtained. Naphthalenone III, prepd. from 2-(2,4-pentadienyl)-1,3-dioxane with Me vinyl ketone and hydrolysis with HClO4, was condensed with a phthalidesulfone through Michael type reaction and the product converted to the epoxide IV by epoxidn. Epoxide IV was transformed to a trione using redn.-oxidn. or hydrofluorination process, and then to I by introducing several functional groups. III was converted to II in two steps.
IT **243843-81-4P**
RL: **RCT (Reactant)**; SPN (Synthetic preparation); **PREP (Preparation)**
(synthesis of 11-deoxydaunomycinone and novel 10-fluoroanthracyclinone derivs.)
RN 243843-81-4 CAPLUS
CN Ethanone, 1-[2-(1,3-dioxan-2-ylmethyl)-3-cyclohexen-1-yl]- (9CI) (CA INDEX NAME)



REFERENCE COUNT: 23
REFERENCE(S):
(2) Arcamone, F; J Am Chem Soc 1980, V102, P1462 CAPLUS
(3) Boeckman, R; J Am Chem Soc 1982, V104, P4604 CAPLUS
(5) Hauser, F; J Org Chem 1983, V48, P1328 CAPLUS
(6) Hauser, F; J Org Chem 1989, V54, P5110 CAPLUS
(7) Hauser, F; Tetrahedron 1984, V40, P4711 CAPLUS
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L19 ANSWER 3 OF 10 CAPLUS COPYRIGHT 2001 ACS (Continued)

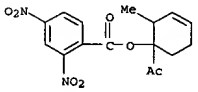
Relative stereochemistry.



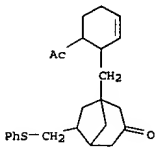
L19 ANSWER 3 OF 10 CAPLUS COPYRIGHT 2001 ACS
ACCESSION NUMBER: 1998:85141 CAPLUS
DOCUMENT NUMBER: 128:192251
TITLE: Conformationally switched-on polyether ionophores
AUTHOR(S): Raban, Morton; Quin, John, III; Belguise, Alain; Durocher, David; Kost, Daniel
CORPORATE SOURCE: Department of Chemistry, Wayne State University, Detroit, MI, 48322, USA
SOURCE: Chirality (1998), 10(1/2), 78-87
CODEN: CHRLEP; ISSN: 0899-0042
PUBLISHER: Wiley-Liss, Inc.
DOCUMENT TYPE: Journal
LANGUAGE: English
AB The syntheses of two types of conformationally switched podand ionophores and their ionophoric properties are described. Both feature cyclohexane rings with polyether groups as trans 1,2 substituents. In the "switched off" forms of the ionophores, the two podand substituents are constrained to a diaxial orientation and cannot chelate a metal ion. In both cases, a chem. reaction, hydrolysis of a ketone acetal, is used to remove the constraint allowing the two podand substituents to achieve a diequatorial orientation. In this conformation, the two diequatorial podand substituents can chelate a potassium ion and the ionophoric properties are "switched on.". In one case, the chains can be held in the diaxial orientation by a large group, an acetyl group derivatized as the ethylene glycol acetal, in the 4 position. When the size of the group is lowered, the polyether groups become equatorial and can complex a potassium ion as evidenced by a conformational change measured by low temp. NMR spectroscopy. In the second example, an annulated ring holds the cyclohexane ring rigidly in the non-complexing conformation. When the restraint is removed, complexation can occur as evidenced by transport of potassium picrate through a liq. membrane (chloroform layer). In both cases, the ionophoric properties are "switched on" by hydrolysis of a ketone acetal.
IT **7353-76-6**, 4-Acetylcyclohexene
RL: **RCT (Reactant)**
(conformationally switched-on polyether ionophores)
RN 7353-76-6 CAPLUS
CN Ethanone, 1-(3-cyclohexen-1-yl)- (9CI) (CA INDEX NAME)

IT **133146-43-7P**
RL: PEP (Physical, engineering or chemical process); PRP (Properties); SPN (Synthetic preparation); **PREP (Preparation)**; PROC (Process)
(switched on ionophore; conformationally switched-on polyether ionophores)
RN 133146-43-7 CAPLUS
CN Ethanone, 1-[3,4-bis[2-(2-ethoxyethoxy)ethoxy]cyclohexyl]-, (1.alpha.,3.beta.,4.alpha.)- (9CI) (CA INDEX NAME)

L19 ANSWER 4 OF 10 CAPLUS COPYRIGHT 2001 ACS
ACCESSION NUMBER: 1997:522227 CAPLUS
DOCUMENT NUMBER: 127:234236
TITLE: .alpha.-Acetyl- and .alpha.-cyanovinyl 2,4-dinitrophenylcarboxylate as useful ketene equivalents for the Diels-Alder reaction
AUTHOR(S): MaGee, David I.; Lee, May Ling
CORPORATE SOURCE: Department Chemistry, University New Brunswick, Fredericton, NB, E3B 6E2, Can.
SOURCE: Synlett (1997), (7), 786-788
CODEN: SYNLES; ISSN: 0936-5214
PUBLISHER: Thieme
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 127:234236
AB The title ketene equiv. were developed for use in the Diels-Alder reaction. These dienophiles exhibit a marked increase in reactivity in comparison with the more conventional AcOC(:CH2)CN. Conversion of the cycloadducts to the requisite ketones occurs under mild, and moderate to high yielding conditions.
IT **195200-19-2P**
RL: **RCT (Reactant)**; SPN (Synthetic preparation); **PREP (Preparation)**
(Diels-Alder reaction with acetyl- and cyanovinyl dinitrophenylcarboxylate as ketene equiv.)
RN 195200-19-2 CAPLUS
CN Ethanone, 1-[1-[(2,4-dinitrobenzoyl)oxy]-2-methyl-3-cyclohexen-1-yl]- (9CI) (CA INDEX NAME)

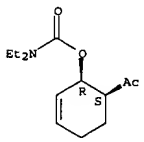


L19 ANSWER 5 OF 10 CAPLUS COPYRIGHT 2001 ACS
ACCESSION NUMBER: 1994:579904 CAPLUS
DOCUMENT NUMBER: 121:179904
TITLE: Bridgehead intermediates in organic synthesis construction of the tetracyclic skeleton of leucothol A
AUTHOR(S): Kraus, George A.; Su, Qiaogong
CORPORATE SOURCE: Dep. Chem., Iowa State Univ., Ames, IA, 50011, USA
SOURCE: Synlett (1994), (4), 237
CODEN: SYNLES; ISSN: 0936-5214
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 121:179904
AB Tetracyclic intermediate I for the synthesis of leucothol A II can be constructed in seven steps. The key step involves the reaction of pentadienyltributylstannane with a bridgehead radical generated from bromide III to give tetracycle I. The crystal structure of I was detd.
IT **157636-09-4P**
RL: **RCT (Reactant)**; SPN (Synthetic preparation); **PREP (Preparation)**
(prepn. and aldol condensation of, leucothol A key intermediate from)
RN 157636-09-4 CAPLUS
CN Bicyclo[3.2.1]octan-3-one, 1-[(6-acetyl-2-cyclohexen-1-yl)methyl]-6-[(phenylthio)methyl]- (9CI) (CA INDEX NAME)



L19 ANSWER 6 OF 10 CAPLUS COPYRIGHT 2001 ACS
ACCESSION NUMBER: 1990:552772 CAPLUS
DOCUMENT NUMBER: 113:152772
TITLE: O-1-(1,3-Butadienyl) carbamates as Diels-Alder dienes:
stereospecific synthesis of (.+-.)-hernandulcin and congeners
AUTHOR(S): De Cusati, Paul F.; Olofson, R. A.
CORPORATE SOURCE: Dep. Chem., Pennsylvania State Univ., University Park,
PA, 16802, USA
SOURCE: Tetrahedron Lett. (1990), 31(10), 1409-12
CODEN: TELEAY; ISSN: 0040-4039
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 113:152772
AB The TiCl4-catalyzed addn. of the title reactants, e.g., RCO2CH:CHCH:CH2 (R
= OEt, NEt2) to vinyl ketones, e.g., MeCOCH:CH2, regio- and stereospecifically yields cis-disubs. cyclohexenes I which add RMgX stereospecifically to the ketone. A final product in this sequence is the
intensely sweet sesquiterpene, hernandulcin (II).
IT **129436-52-8P**
RL: **RCT (Reactant)**; SPN (Synthetic preparation); **PREP (Preparation)**
(prepn. and Grignard reaction of, with methylpentenylmagnesium bromide)
RN 129436-52-8 CAPLUS
CN Carbamic acid, diethyl-, 6-acetyl-2-cyclohexen-1-yl ester, cis- (9CI) (CA
INDEX NAME)

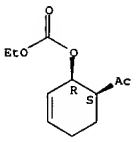
Relative stereochemistry.



IT **129447-03-6P**
RL: SPN (Synthetic preparation); **PREP (Preparation)**
(prepn. of, via Diels-alder reaction of butadienyl carbonate with butenone)
RN 129447-03-6 CAPLUS
CN Carbonic acid, 6-acetyl-2-cyclohexen-1-yl ethyl ester, cis- (9CI) (CA INDEX NAME)

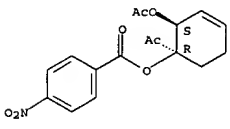
Relative stereochemistry.

L19 ANSWER 6 OF 10 CAPLUS COPYRIGHT 2001 ACS (Continued)



L19 ANSWER 7 OF 10 CAPLUS COPYRIGHT 2001 ACS
ACCESSION NUMBER: 1990:97817 CAPLUS
DOCUMENT NUMBER: 112:97817
TITLE: Highly selective Diels-Alder cycloadditions of captodative dienophiles 1-acetylvinyl arenecarboxylates to unsymmetrically substituted butadienes
AUTHOR(S): Reyes, Alicia; Aguilar, Raul; Munoz, Alfredo H.; Zwick, Jean Christophe; Rubio, Manuel; Escobar, Jose Luis; Soriano, Manuel; Toscano, Ruben; Tamariz, Joaquin
CORPORATE SOURCE: Esc. Nac. Cienc. Biol., IPN, Mexico City, 11340, Mex.
SOURCE: J. Org. Chem. (1990), 55(3), 1024-34
CODEN: JOCEAH; ISSN: 0022-3263
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 112:97817
AB Thermal Diels-Alder cycloaddns. of captodative olefins 1-acetylvinyl arenecarboxylates, CH2:C(COCH3)OCOAr (Ar = p-C6H4NO2, .alpha.-naphthyl and
.beta.-naphthyl), with isoprene were regioselective. This regioselectivity was greatly improved by using Lewis acids catalysts (ZnCl2, BF3.cntdot.Et2O), the para adduct being the main isomer. Stereoselectivity of these reactions was examd. Regioselectivity of these
cycloaddns. has been rationalized by MINDO/3 and ab initio methods.
IT **111945-70-1P 111945-71-2P**
RL: **RCT (Reactant)**; SPN (Synthetic preparation); **PREP (Preparation)**
(prepn. and hydrolysis of)
RN 111945-70-1 CAPLUS
CN Ethanone, 1-[2-(acetyloxy)-1-[(4-nitrobenzoyl)oxy]-3-cyclohexen-1-yl]-, cis- (9CI) (CA INDEX NAME)

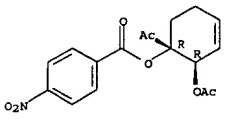
Relative stereochemistry.



RN 111945-71-2 CAPLUS
CN Ethanone, 1-[(1R,2R)-2-(acetyloxy)-1-[(4-nitrobenzoyl)oxy]-3-cyclohexen-1-yl]-, rel- (9CI) (CA INDEX NAME)

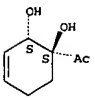
Relative stereochemistry.

L19 ANSWER 7 OF 10 CAPLUS COPYRIGHT 2001 ACS (Continued)



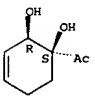
IT **125229-00-7P 125229-01-8P**
RL: **RCT (Reactant)**; SPN (Synthetic preparation); **PREP (Preparation)**
(prepn. and ketalization of)
RN 125229-00-7 CAPLUS
CN Ethanone, 1-[(1R,2R)-1,2-dihydroxy-3-cyclohexen-1-yl]-, rel- (9CI) (CA INDEX NAME)

Relative stereochemistry.



RN 125229-01-8 CAPLUS
CN Ethanone, 1-(1,2-dihydroxy-3-cyclohexen-1-yl)-, cis- (9CI) (CA INDEX NAME)

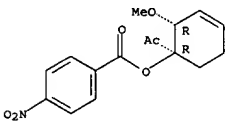
Relative stereochemistry.



IT **111945-72-3P 111945-73-4P 111945-74-5P**
111945-75-6P 125229-07-4P
RL: SPN (Synthetic preparation); **PREP (Preparation)**
(prepn. of)
RN 111945-72-3 CAPLUS
CN 2-Cyclohexene-1-carboxylic acid, 6-acetyl-6-[(4-nitrobenzoyl)oxy]-, methyl
ester, cis- (9CI) (CA INDEX NAME)

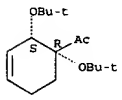
Relative stereochemistry.

L19 ANSWER 7 OF 10 CAPLUS COPYRIGHT 2001 ACS (Continued)

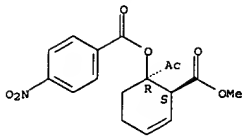


RN 125229-07-4 CAPLUS
CN Ethanone, 1-[1,2-bis(1,1-dimethylethoxy)-3-cyclohexen-1-yl]-, cis- (9CI) (CA INDEX NAME)

Relative stereochemistry.

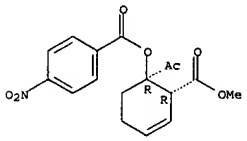


L19 ANSWER 7 OF 10 CAPLUS COPYRIGHT 2001 ACS (Continued)



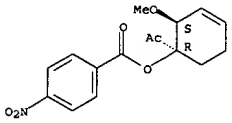
RN 111945-73-4 CAPLUS
CN 2-Cyclohexene-1-carboxylic acid, 6-acetyl-6-[(4-nitrobenzoyl)oxy]-, methyl
ester, (1R,6R)-rel- (9CI) (CA INDEX NAME)

Relative stereochemistry.



RN 111945-74-5 CAPLUS
CN Ethanone, 1-[2-methoxy-1-[(4-nitrobenzoyl)oxy]-3-cyclohexen-1-yl]-, cis- (9CI) (CA INDEX NAME)

Relative stereochemistry.



RN 111945-75-6 CAPLUS
CN Ethanone, 1-[2-methoxy-1-[(4-nitrobenzoyl)oxy]-3-cyclohexen-1-yl]-, trans-
(9CI) (CA INDEX NAME)

Relative stereochemistry.

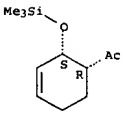
L19 ANSWER 8 OF 10 CAPLUS COPYRIGHT 2001 ACS

ACCESSION NUMBER:	1989:458056 CAPLUS
DOCUMENT NUMBER:	111:58056
TITLE:	Total synthesis of various elemanolides
AUTHOR(S):	Friedrich, Dirk; Bohlmann, Ferdinand
CORPORATE SOURCE:	Inst. Org. Chem., Tech. Univ. Berlin, Berlin, D-1000/12, Fed. Rep. Ger.
SOURCE:	Tetrahedron (1988), 44(5), 1369-92 CODEN: TETRAB; ISSN: 0040-4020
DOCUMENT TYPE:	Journal
LANGUAGE:	English
OTHER SOURCE(S):	CASREACT 111:58056

AB Starting with suitably substituted divinyl cyclohexanone I, 11 naturally occurring 12.8-elemanolides bearing exo-methylene or Me groups at C(11) and differing in substitution as well as in relative configuration, were synthesized in racemic form. An approach to elemanolides with addnl. oxygen functionalities is possible by modification of the basic concept. Methods for the oxidative generation of terpenoid exo-methylene lactone and furan units are exemplified by synthesis of menthofuran (II) and the p-menthenolides (III) from isopulegols (IV).

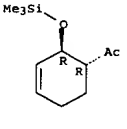
IT **121401-44-3P 121401-45-4P**
RL: **RCT (Reactant)**; SPN (Synthetic preparation); **PREP (Preparation)**
(prepn. and Wittig reaction of, with methylidenetriphenylphosphorane)
RN 121401-44-3 CAPLUS
CN Ethanone, 1-[2-[(trimethylsilyl)oxy]-3-cyclohexen-1-yl]-, cis- (9CI) (CA INDEX NAME)

Relative stereochemistry.



RN 121401-45-4 CAPLUS
CN Ethanone, 1-[2-[(trimethylsilyl)oxy]-3-cyclohexen-1-yl]-, trans- (9CI) (CA INDEX NAME)

Relative stereochemistry.



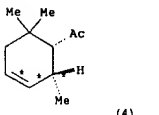
=> d ibib ab hit 1-2

L15 ANSWER 1 OF 2 CASREACT COPYRIGHT 2003 ACS
ACCESSION NUMBER: 136:20169 CASREACT
TITLE: Process for production of cyclohexenyl methyl ketones as intermediates for perfumery damascones
INVENTOR(S): Watanabe, Shinya; Ujihara, Hideo; Yamamoto, Takeshi; Hagiwara, Toshimitsu
PATENT ASSIGNEE(S): Takasago International Corporation, Japan
SOURCE: Eur. Pat. Appl., 12 pp.
CODEN: EPXXDW
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
EP 1162190	A2	20011212	EP 2001-401471	20010607
EP 1162190	A3	20020130		
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO				
JP 2001348355	A2	20011218	JP 2000-170823	20000607
US 2002004615	A1	20020110	US 2001-875158	20010607

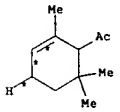
PRIORITY APPLN. INFO.: JP 2000-170823 20000607
OTHER SOURCE(S): MARPAT 136:20169
AB An economical process for producing (2- and/or 1-)cyclohexenyl Me ketones which are intermediates for the synthesis of .alpha.- or .beta.-damascone. In the presence of a catalyst, a 3-cyclohexenyl Me ketone (I) (R1, R2 and R3 each independently = H, Me and at least two of R1, R2 and R3 = Me), is isomerized.

RX(4) OF 13 ...O ===> A...



O

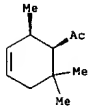
(4)



A
YIELD 87%

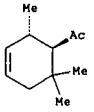
L15 ANSWER 2 OF 2 CASREACT COPYRIGHT 2003 ACS
ACCESSION NUMBER: 119:203029 CASREACT
TITLE: Preparation and scent of .delta.-damascone and its analogs
AUTHOR(S): Andreev, V. M.; Andreeva, L. K.; Ratnikova, E. V.; Fomchenko, Z. V.; Grigor'eva, L. T.
CORPORATE SOURCE: VNII Sint. Nat. Dushistykh Veshchestr, Russia
SOURCE: Gidroliznaya i Lesokhimicheskaya Promyshlennost (1993), (1), 23-4
CODEN: GLKPA2; ISSN: 0016-9706
DOCUMENT TYPE: Journal
LANGUAGE: Russian
AB Diels-Alder reaction of CH2:CRCH:CHR1 (R = H, R1 = H, Me; R = Me, R1 = H) with 5 equiv MeCOCR2:CMeR3 (R2 = H, R3 = Me; R2 = Me, R3 = H) in PhMe contg. 5 mol% AlCl3 at 35-40.degree. gave .ltoreq.81% yields of 5 corresponding acetylcyclohexene adducts I (R4 = Me). These underwent aldol condensation with MeCHO and subsequent dehydration to give .ltoreq.48% title compds. I (same R-R3, R4 = CH:CHMe). These products had fruity, woody, or camphor-like odors with spicy or vegetable notes.

RX(3) OF 7 ...I ===> A...



I

(3)



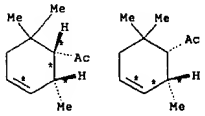
A
YIELD 100%

RX(3) RCT I **41436-48-0**
RGT L 1310-58-3 KOH
PRO A **41435-93-2**
SOL 64-17-5 EtOH

L15 ANSWER 1 OF 2 CASREACT COPYRIGHT 2003 ACS (Continued)

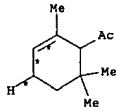
RX(4) RCT O **41436-48-0**
PRO A **37709-66-3**
CAT 13569-65-8 Rhodium chloride (RhCl3), trihydrate
SOL 64-17-5 EtOH
NTE alternative prepns. gave lower yields

RX(5) OF 13 ...2 O ===> A + K...

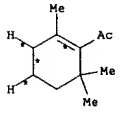


O O

(5)



A
YIELD 43%



K
YIELD 27%

RX(5) RCT O **41436-48-0**
RGT S 294-62-2 Cyclododecane
PRO A **37709-66-3**, K **1197-92-8**
CAT 1907-33-1 Li tert-butoxide
SOL 127-19-5 AcNMe2
NTE alternative prepns. gave lower yields

=> d ibib ab hitstr

L33 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 2001:900120 CAPLUS
DOCUMENT NUMBER: 136:20169
TITLE: Process for production of cyclohexenyl methyl ketones as intermediates for perfumery damascones
INVENTOR(S): Watanabe, Shinya; Ujihara, Hideo; Yamamoto, Takeshi; Hagiwara, Toshimitsu
PATENT ASSIGNEE(S): Takasago International Corporation, Japan
SOURCE: Eur. Pat. Appl., 12 pp.
CODEN: EPXXDW
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
EP 1162190	A2	20011212	EP 2001-401471	20010607
EP 1162190	A3	20020130		
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO				
JP 2001348355	A2	20011218	JP 2000-170823	20000607
US 2002004615	A1	20020110	US 2001-875158	20010607

PRIORITY APPLN. INFO.: JP 2000-170823 A 20000607
OTHER SOURCE(S): CASREACT 136:20169; MARPAT 136:20169

AB An economical process for producing (2- and/or 1-)cyclohexenyl Me ketones which are intermediates for the synthesis of .alpha.- or .beta.-damascone. In the presence of a catalyst, a 3-cyclohexenyl Me ketone (I) (R1, R2 and R3 each independently = H, Me and at least two of R1, R2 and R3 = Me), is isomerized.

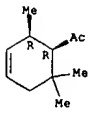
IT **1197-92-8P 41436-48-0P**
RL: IMF (Industrial manufacture); **RCT (Reactant)**; SPN (Synthetic preparation); **PREP (Preparation)**; RACT (Reactant or reagent)
(process for prodn. of cyclohexenyl Me ketones as intermediates for perfumery damascones)

RN 1197-92-8 CAPLUS
CN Ethanone, 1-(2,6,6-trimethyl-1-cyclohexen-1-yl)- (9CI) (CA INDEX NAME)

RN 41436-48-0 CAPLUS
CN Ethanone, 1-[(1R,2R)-2,6,6-trimethyl-3-cyclohexen-1-yl]-, rel- (9CI) (CA INDEX NAME)

Relative stereochemistry.

L33 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2003 ACS (Continued)



=> d ibib ab hitstr 1-2

L41 ANSWER 1 OF 2 USPATFULL
ACCESSION NUMBER: 2002:8615 USPATFULL
TITLE: Production process of cyclohexenyl ketones
INVENTOR(S): Watanabe, Shinya, Kanagawa, JAPAN
Ujihara, Hideo, Kanagawa, JAPAN
Yamamoto, Takeshi, Kanagawa, JAPAN
Hagiwara, Toshimitsu, Kanagawa, JAPAN
PATENT ASSIGNEE(S): TAKASAGO INTERNATIONAL CORPORATION (non-U.S. corporation)

	NUMBER	KIND	DATE
PATENT INFORMATION:	US 2002004615	A1	20020110
APPLICATION INFO.:	US 2001-875158	A1	20010607 (9)

	NUMBER	DATE
PRIORITY INFORMATION:	JP 2000-170823	20000607

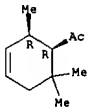
DOCUMENT TYPE: Utility
FILE SEGMENT: APPLICATION
LEGAL REPRESENTATIVE: SUGHRUE, MION, ZINN,, MACPEAK & SEAS, PLLC, 2100 Pennsylvania Avenue, NW, Washington, DC, 20037-3213
NUMBER OF CLAIMS: 5
EXEMPLARY CLAIM: 1
LINE COUNT: 524
CAS INDEXING IS AVAILABLE FOR THIS PATENT.
AB An economical process for producing (2- and/or 1-)cyclohexenyl methyl ketones which are intermediates for the synthesis of .alpha.- or .beta.-damascone. In the presence of a catalyst, a 3-cyclohexenyl methyl ketone represented by the following formula (1a): ##STR1##

wherein, R.sub.1, R.sub.2 and R.sub.3 each independently represents a hydrogen atom or a methyl group and at least two of R.sub.1, R.sub.2 and R.sub.3 are methyl groups, is isomerized.
IT **1197-92-8P 41436-48-0P**
(process for prodn. of cyclohexenyl Me ketones as intermediates for perfumery damascones)
RN 1197-92-8 USPATFULL
CN Ethanone, 1-(2,6,6-trimethyl-1-cyclohexen-1-yl)- (9CI) (CA INDEX NAME)

RN 41436-48-0 USPATFULL
CN Ethanone, 1-[(1R,2R)-2,6,6-trimethyl-3-cyclohexen-1-yl]-, rel- (9CI) (CA INDEX NAME)

Relative stereochemistry.

L41 ANSWER 1 OF 2 USPATFULL (Continued)



L41 ANSWER 2 OF 2 USPATFULL
ACCESSION NUMBER: 97:81056 USPATFULL
TITLE: Simulated photographic-quality prints using a plasticizer to reduce curl
INVENTOR(S): Malhotra, Shadi L., Ontario, Canada
PATENT ASSIGNEE(S): Xerox Corporation, Stamford, CT, United States (U.S. corporation)

	NUMBER	KIND	DATE
PATENT INFORMATION:	US 5665504		19970909
APPLICATION INFO.:	US 1996-584784		19960111 (8)

DOCUMENT TYPE: Utility
FILE SEGMENT: Granted
PRIMARY EXAMINER: Rodee, Christopher D.
NUMBER OF CLAIMS: 20
EXEMPLARY CLAIM: 1
NUMBER OF DRAWINGS: 2 Drawing Figure(s); 2 Drawing Page(s)
LINE COUNT: 1967
CAS INDEXING IS AVAILABLE FOR THIS PATENT.
AB Simulated photographic-quality prints are created using nonphotographic imaging such as xerography and ink jet. Reverse or wrong reading toner images are formed on a transparent subs,trate which is adhered to a coated backing sheet. The backing sheet is coated with a polymer material which serves as an adhesive and has a glass transition temperature less than 55.degree. C. A hydrophilic polymer coating having a melting point greater than 50.degree. C and a toner plasticizer having a melting point less than 75.degree. C contacting the adhesive polymer serves as a wetting agent for providing an enhanced optical interface as well as protection for the adhesive polymer which has a lower melting point than the adhesive polymer.
IT **932-66-1**, 1-Acetyl-1-cyclohexene **6090-09-1**, 4-Acetyl-1-methylcyclohexene
(simulated photog.-quality prints contg.)
RN 932-66-1 USPATFULL
CN Ethanone, 1-(1-cyclohexen-1-yl)- (9CI) (CA INDEX NAME)

RN 6090-09-1 USPATFULL
CN Ethanone, 1-(4-methyl-3-cyclohexen-1-yl)- (9CI) (CA INDEX NAME)